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THE SYSTEM STRONTIUM-BISMUTH

S. A. Shchukarev, M. P. Morozova, Kan Kho-Yn and G. V. Kokosh

We have examined the system strontium-bismuth (no data about which have appeared in the literature) as part of a scheme for systematic investigation of the forms and enthalpies of formation of compounds of elements of the principal subgroup of Group V with alkali and alkaline earth metals. In this connection we were not interested in the details of the phase diagram of this system (composition of eutectics, occurrence of polymorphic transformations, etc.); our objective was solely the establishment of the types of compounds formed by strontium with bismuth. We applied three methods: plotting of cooling curves and construction of the fusion diagram; investigation of the microstructure; investigation of the change in molecular volumes with composition (expressed in atom percentages).

The strontium required for the investigation was prepared by high-vacuum alumothermy. The bismuth was the grade sold as "pure for analysis". For plotting of cooling curves, a definite amount of the alloy was placed in an iron crucible supported on two quartz tubes through the joint of which was inserted a chromel-alumel thermocouple. The hot junction of the thermocouple terminated in a small thin-walled iron tube. After evacuation to high vacuum, the quartz tube was thoroughly purged with argon; the experiments were also conducted in an argon atmosphere. Densities were determined in a vacuum pycnometer; kerosene served as the sealing liquid.

The temperatures of primary crystallization and of crystallization of eutectics, also the duration of the eutectic halts, are set forth in Table 1.

TABLE 1

Sr content (at. %)	Temperature of primary crystallization	Eutectic or peritectic halt	
		temperature	duration (in sec.)
5	311°	262°	150
10	408.8	261.8	120
15	494.5	261.5	60
20	541.9	261.9	30
25	632	—	—
27	617	580	180
30	632	583	150
(40)	720	585	60
40	720	720	0
45	775	721	60
50	835.5	719.5	120
55	915	723	60
60	946	—	—
63	914	813	180
67	858	—	—
75	816.7	661.7	60
80	750	661	90
90	669.5	657.5	120
95	733.5	662.5	60

The fusion diagram is presented in the upper part of Fig. 1. The cooling curves of alloys containing 5, 10, 15 and 20 at. % strontium exhibit a discontinuity, associated with primary crystallization, and a halt corresponding to crystallization of the eutectic. The eutectic halt is absent from the cooling curve of the alloy containing 25 at. % strontium, and the maximum on the liquidus curve corresponds to this composition. We can therefore assume the existence of a congruently melting (at 632°) compound $SrBi_3$. The cooling curve of the alloy containing 27 at. % strontium exhibits a halt corresponding to crystallization of the eutectic. With rising content of strontium the liquidus curve falls until the strontium content is 60 at. %, at which point a sharp maximum appears on the liquidus curve at 945°. On the cooling curves of alloys with 45, 50 and 55 at. % strontium, apart from discontinuities corresponding to primary crystallization, there is a halt at 719°. Its maximum duration is observed at 50 at. % strontium. The occurrence of this halt points to the existence of an incongruently melting compound SrBi. This halt is absent from the cooling curve of the alloy containing 60 at. % strontium.

Apart from an inflection corresponding to primary crystallization, the cooling curve of the alloy containing

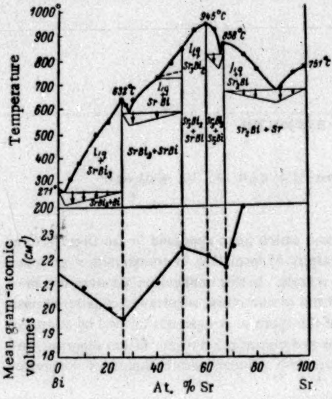

Fig. 1. Fusion diagram and change of mean gram-atomic volumes in the system strontium-bismuth.

TABLE 2

Sr content (atom %)	Mean atomic weight	Density	Mean atomic volume (in cc)
10	196.86	9.43	20.8
20	184.72	9.25	19.9
25	178.66	9.15	19.5
30	172.58	8.64	20.0
40	160.45	7.64	20.9
50	148.31	6.61	22.4
60	136.18	6.17	22.0
67	127.68	5.91	21.6
70	124.04	5.52	22.4
80	111.90	4.64	24.1
90	99.76	3.63	27.4

63 at. % strontium exhibits a halt at 813°. On the basis of the change in mean gram-atomic volumes in the system strontium-bismuth (Fig. 1), we can regard this halt as a eutectic halt corresponding to the common crystallization of the compounds Sr_3Bi_2 and Sr_2Bi.

On the cooling curves of alloys with 75, 80, 90 and 95 at. % strontium, a eutectic halt is present at 659°, corresponding to the common crystallization of Sr_2Bi and Sr. This halt is absent from the cooling curve of the alloy of composition Sr_2Bi, thus confirming the existence of the compound Sr_2Bi. The eutectic Sr_2Bi-Sr lies at approximately 88 at. % strontium.

In Table 2 are set forth the results of measurement of the density and of mean atomic volumes obtained on the basis of the density value.

It should be noted that the fairly large deviations in the values of the density are due to the difficulties of working with such reactive substances as alloys of strontium and bismuth. The course of the atomic volumes (Fig. 1) points to the existence of the compounds $SrBi_3$, SrBi, Sr_3Bi_2 and Sr_2Bi, thus confirming the picture obtained by thermal analysis.

Photographs of the microsections, obtained by polishing under thoroughly dried kerosene, are presented in Fig. 2 (a-g).

The alloy containing 1 at. % strontium is homogeneous. This is evidently close to the eutectic. On the photographs of the sections with 5, 10, 15 and 20 at. % strontium, the originally formed crystals of $SrBi_3$ and the eutectic (white field) are clearly visible. The amount of eutectic progressively decreases. The microsection of the alloy with 25 at. % strontium ($SrBi_3$) is homogeneous, as was to be expected on the basis of the fusion diagram and of the course of the mean atomic volumes. Concerning the microsections of alloys with a higher strontium content, these were quite convenient for visual inspection under the microscope, but their photographs were unsharp due to corrosion of the alloy taking place on long exposure; they are therefore not reproduced here. Visual examination of the polished sections with 30 and 40 at. % strontium reveals the presence of two phases. Alloys containing 50, 60 and 70 at. % strontium are homogeneous in the first moment of their inspection. On the sections of alloys containing 90 and 95 at. % the crystals characteristic of metallic strontium were clearly visible against the background of the eutectic. This indicates that strontium is the phase primarily crystallizing from alloys of this composition. Consequently, the existence of the compounds $SrBi_3$, SrBi, Sr_3Bi_2 and Sr_2Bi is indicated in the system strontium-bismuth by all the three methods of physicochemical analysis utilized by us.

The existence of two compounds has been established in the system calcium-bismuth: the incongruently melting $CaBi_3$ and the congruently melting Ca_3Bi_2 [1].

G. Grube and A. Dietrich [2] attempted to investigate the system barium-bismuth. The low thermal effects prevented these authors from using the method of thermal analysis for alloys containing more than 21% barium (they did no apply other methods for investigation of this system). In the investigated region of compositions they found the incongruently melting compound $BaBi_3$. Thus the existence of a compound of the form of $Me^{II}Bi_3$ is characteristic of all systems of alkaline earth metal-bismuth.

Comparison of the system strontium-bismuth with the system calcium-bismuth reveals an increase in the number of thermodynamically stable compounds. It is necessary to point out that this is also characteristic of systems of these elements with non-metals. Thus, strontium forms two thermodynamically stable oxygenated compounds SrO and SrO_2, whereas calcium forms only one (CaO). With nitrogen, strontium forms Sr_3N_2 and Sr_2N, whereas calcium forms only the usual nitride Ca_3N_2 [3]. In the case of compounds related to ionic compounds (oxides, nitrides), the increase of stability of per- and hypo- compounds in passing from calcium to strontium and barium may be interpreted as the result of decrease of the energy necessary for loosening the lattice of the compound of normal form; this loosening is required for introduction into the lattice of certain atoms. The fall in energy of loosening of the lattice is accounted for by the increase in ionic radii in the direction Ca → Ba.

Compounds of metals of the main subgroup of Groups I and II of the periodic system with bismuth resemble salt-formers in some degree, as pointed out by Zintl [4]. It is therefore possible that the increase in the number of compounds in the system Sr-Bi, compared with the system Ca-Bi, can also be due to decrease of the lattice energy of compounds corresponding to the normal valences of the components (Sr_3Bi_2).

The compounds SrBi, Sr_3Bi_2 and Sr_2Bi react violently with dilute hydrochloric acid; $SrBi_3$ harly reacts even with concentrated acid. We made use of the reaction of the first three compounds with dilute (1 N) HCl for determination of their enthalpies of formation.

The procedure for calorimetric determinations has been described earlier [5].

The following enthalpies of formation were found from a series of calorimetric experiments carried out with specimens of the different alloys:

$$\text{SrBi: } \Delta H_{form} = -43.0 \pm 2.7 \text{ kcal/mole,}$$

$$Sr_{cr} + Bi_{cr} = SrBi_{cr} + 43.0 \pm 2.7 \text{ kcal.}$$

$$Sr_3Bi_2\text{: } \Delta H_{form} = -126.8 \pm 2.6 \text{ kcal/mole,}$$

$$3Sr_{cr} + 2Bi_{cr} = Sr_3Bi_{2\,cr} + 126.8 \pm 2.6 \text{ kcal.}$$

$$Sr_2Bi\text{: } \Delta H_{form} = -74.8 \pm 1.2 \text{ kcal/mole}$$

$$2Sr_{cr} + Bi_{cr} = Sr_2Bi + 74.8 \pm 1.2 \text{ kcal}$$

In Fig. 3 the magnitudes of the enthalpies of formation of these compounds, related to one mean gram-atom (i.e. the enthalpies of formation per gram-mole divided by number of atoms of both elements in the fomula) are plotted as a function of composition. Weibke and Kubaschewski [6] and also Dehlinger [7] point out that the heats of formation of compounds of two metals sharply differing from one another in chemical properties are characterized by the fact that the maximum of the heats of formation, related to the mean gram-atom, occurs with the compound whose form corresponds to the normal valences of both elements; on both sides of this maximum the heats of formation lie on straight lines connecting the vertex with the corners of the diagram. The above authors correlate this course of the heats of formation with the change in ionic character of the bonds with changing composition. We have pointed out [8] that this regularity is not exactly valid in the general case and that it may be explained from a more general standpoint not involving hypotheses about the change of character of the bonds.

In the system Sr-Bi the enthalpies of formation of SrBi and Sr_3Bi_2 conform to this regularity. The enthalpy of formation of Sr_2Bi is higher than would be expected on the basis of the rule in question.

In Fig. 4 the enthalpies of formation are plotted against the mean composition in gram-atoms for the system Ba-N [9]. It is interesting that in this system, just as in the system Sr-Bi, the isoatomic values of the enthalpies of formation are similar for the forms Me_3X_2 and Me_2X, where X is nitrogen or bismuth.

Fig. 5 is a plot of the dependence of the contraction, occurring during formation of compounds from elements, on the composition of the compounds. A comparison of Figs. 3 and 5 reveals that the unexpectedly high heat of formation of the compound Sr_2Bi corresponds also to the maximum contraction of this form.

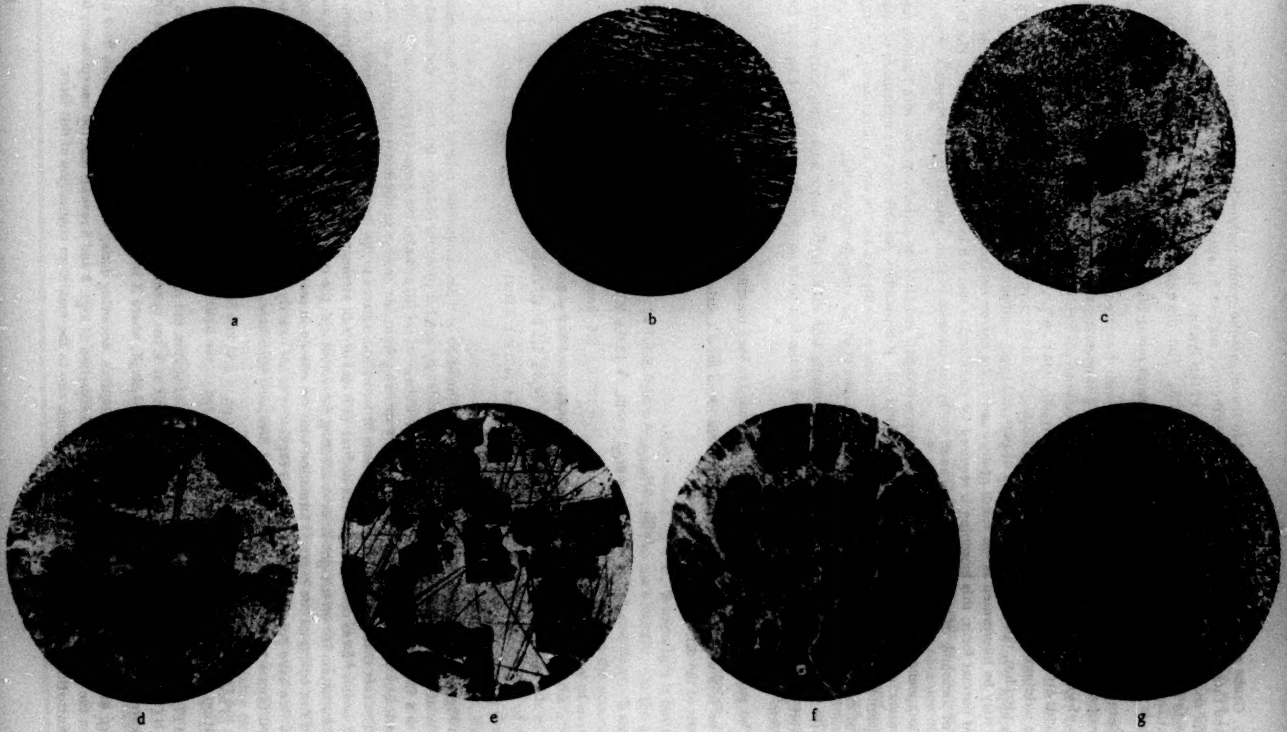

Fig. 2. Photomicrographs of polished sections.
a) bismuth; b) alloy with 1 at.-% strontium; c) alloy with 2 at.-% strontium; d) alloy with 5 at.-% strontium; e) alloy with 10 at.-% strontium; f) alloy with 20 at.-% strontium; g) alloy with 25 at.-% strontium.

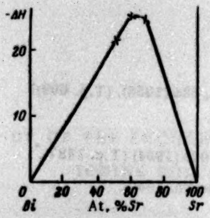

Fig. 3. Dependence of ethalpy of formation of compounds in the system strontium-bismuth (per 1 mean gram-atom) on composition.

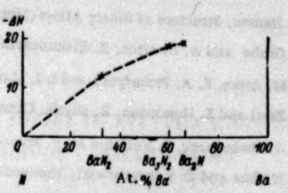

Fig. 4. Dependence of enthalpy of formation of compounds in the system barium-nitrogen on the composition per mean gram-atom.

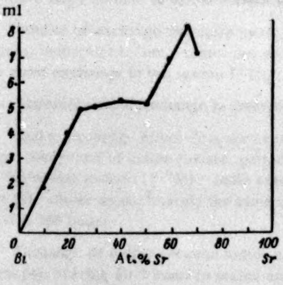

Fig. 5. Contraction in the system strontium-bismuth as a function of the composition.

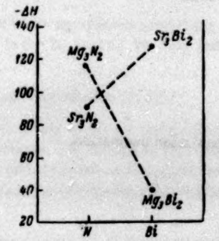

Fig. 6. Enthalpies of formation of compounds of magnesium and strontium with nitrogen and bismuth.

In Fig. 6 a comparison is made of the enthalpies of formation of compounds of magnesium and strontium with elements of the principal subgroup of Group V (for the forms Me_3X_2). A conspicuous difference is apparent: in the case of magnesium the enthalpy of formation of the bismuthide is nearly three times less than the enthalpy of formation of the nitride. But in the case of strontium the enthalpy of formation of the bismuthide is considerably greater than the enthalpy of formation of the nitride.

SUMMARY

1. The existence of the congruently melting compounds $SrBi_3$, Sr_3Bi_2 and Sr_2Bi and of the incongruently melting compound SrBi was established in an investigation of the system Sr-Bi by thermal analysis and from a study of the course of the mean atomic volumes.

2. Microscopic examination of polished sections confirmed the form of the phase diagrams of the system Sr-Bi obtained with the help of the first two methods mentioned.

3. Enthalpies of formation were determined from the magnitudes of the heats of reaction of SrBi, Sr_3Bi_2 and Sr_2Bi with dilute hydrochloric acid.

4. Some regularities of the magnitudes of the enthalpies of formation of binary compounds of elements of the principal subgroup of Group V were noted.

LITERATURE CITED

[1] M. Hansen, Structure of Binary Alloys (Metallurgical Press, 1941).

[2] G. Grube and A. Dietrich, Z. Elektrochem.44, 755 (1938).

[3] S. M. Ariya, E. A. Prokofyeva and I. I. Matveeva, J. Gen. Chem. 25, 634 (1955). (T.p. 609).*

[4] E. Zintl and E. Husemann, Z. physik. Chem. B, 21, 1938 (1933).

[5] S. A. Shchukarev, E. Volf and M. P. Norozova, J. Gen. Chem. 24, 1925 (1954) (T.p. 1887).*

[6] F. Weibke and O. Kubaschewski, Thermochemie der Legierungen (Berlin, 1943).

[7] U. Dehiinger, Umschau Wiss. u. Tech. 53, No. 3 (1953).

[8] S. A. Shchukarev, M. P. Morozora and Yu. P. Sapozhnikov, J. Gen. Chem. 25, 304 (1955) (T.p. 287).*

[9] S. M. Ariya and E. A. Prokofyeva, J. Gen. Chem. 25, 849 (1955) (T.p. 813).*

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STUDY OF THE EXCHANGE REACTIONS OF IODINE IN SYSTEMS CONTAINING IODINE CHLORIDE BY THE METHOD OF LABELED ATOMS

V. L. Pavlov and Yu. Ya. Fialkov

Study of exchange reactions between compounds of one and the same element with different degrees of oxidation are of considerable interest particularly from the standpoint of the possibility of reversible chemical interaction between these compounds. One of the most interesting subjects of such an investigation is iodine since it forms a large number of stable compounds with different degrees of oxidation (-1, +1, 3, 5, 7).

Studies of exchange reactions in all possible oxidation stages of binary systems comprising iodine compounds (iodides, molecular iodine, iodates and periodates) have appeared in the literature. We only failed to find any data about exchange in the system I'-IO_4'.

Extremely rapid exchange is observed in the system I_2-I' in aqueous solution [1, 2].

Iodine exchange either does not occur at all or only goes very slowly in all systems studied that contain an oxygen compound of iodine (iodate, periodate) as one of the components. Thus in an aqueous solution of the system molecular iodine (10^{-3}M) – iodic acid ($5 \cdot 10^{-2}$M) at 25°, the period of half-exchange of iodine is 2,420 hours [3]. Under approximately the same conditions but in 3 N solution of perchloric acid, the half-exchange period is 160 hours.

Exchange of iodine between iodide and iodate in aqueous solution only takes place under fairly drastic conditions [4]: heating for 2 hours in sealed ampoules to 250° in the system I'-IO_3' gave 33% exchange; 4 hours heating resulted in 40% exchange.

According to the data of Cottin and Haissinsky, molecular iodine slowly exchanges in 0.5 N nitric acid solution with periodate [5, 6].*

Very slow exchange of iodine was found between iodate and periodate in 0.02 N nitric acid at 98° (period of half-exchange 100-200 days) [6]. The speed of exchange is greatly increased by introducing molecular iodine into the solution of iodate and periodate [5].

The literature is lacking, however, in any data for exchange in systems in which one of the components could be a compound of monovalent electropositive iodine.

Such data are of interest not only for supplementing our knowledge of the nature of exchange of iodine between its compounds of different valences; the establishment of the occurrence or absence of iodine exchange in systems containing monovalent electropositive iodine enables conclusions to be drawn about the possibility of certain reversible reactions between components of a given system. Thus, for example, iodine in aqueous solution may be expected to combine with iodine chloride to give a compound of the type of a polyiodide:

$$I_2 + ICl \rightleftharpoons [I(I_2)]Cl. \tag{1}$$

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* Our experiments did not confirm the occurrence of exchange in the system I_2-IO_4' reported by these authors: at 18° after 208 hours we did not find exchange of iodine in 5 N sulfuric acid ($I_2 - 5.66 \cdot 10^{-4}$ M; $NaIO_4 - 1.13 \cdot 10^{-3}$ M). Nor was exchange observed in 0.5 N nitric acid after 140 hours under roughly the same conditions of concentrations.

These considerations are based on the fact that the I^+ cation must possess a considerable polarizing activity.

In one case the formation of a complex of the polyiodide type with the I^+ cation as coordination center has already been established: hypoiodous acid is capable of adding on a molecule of iodine to give the so-called hypotriiodic acid [7, 8]:

$$I_2 + IOH = I_3OH.$$

On this basis, Skrabal and Buchta [8] tried to detect a product of addition of iodine to iodine chloride in hydrochloric acid solution, but did not succeed.

On the other hand the failure to isolate this compound in the pure state or to demonstrate its existence by the normal methods of chemical analysis does not prove its non-existence. The compound formed may be very unstable, i.e. the equilibrium ofReaction (1) may be very sharply displaced to the left.

The occurrence of iodine exchange between I_2 and ICl in solution indicates possible formation of an unstable polyiodide – a product of addition of one molecule (or several molecules) of iodine to iodine chloride – in a process similar to the rapid exchange of molecular iodine with iodide which leads to complex formation [1]:

$$I' + \overset{\bullet}{I}_2 \rightleftharpoons [I(\overset{\bullet}{I}_2)]' \rightleftharpoons I'^{\bullet} + I^{\bullet}I.$$

Exchange of iodine between iodine chloride and iodate suggests the possibility in solution of the following irreversible process:

$$I^+ + IO_3' + 6H^+ \rightleftharpoons 2I^{3+} + 3H_2O,$$

similar to the exchange between iodine and iodate in an acid medium [3] which is evidently due to an irreversible reaction:

$$2I_2 + IO_3' + 6H^+ \rightleftharpoons 5I^+ + 3H_2O.$$

For these reasons we selected iodine chloride as the monovalent, electropositive compound of iodine.

Exchange reactions of iodine chloride with molecular iodine, iodate and periodate were studied.

EXPERIMENTAL

Exchange was investigated at 18°. All experiments were performed in 0.4 N hydrochloric acid solution in which iodine chloride is stable and is not hydrolyzed, being present in the form of the complex acid $H(ICl_2)$ [9, 10]. A certain proportion of the latter is liable to dissociate according to the scheme:

$$H[ICl_2] \rightleftharpoons H^+ + [ICl_2]' \rightleftharpoons H^+ + I^+ + 2Cl'.$$

The hydrochloric acid solution of iodine chloride was obtained by the method of A. I. Gengrinovich by reaction of potassium iodide, potassium iodate and hydrochloric acid [9].

For the study of exchange of molecular iodine with iodine chloride, the hydrochloric acid solution of iodine chloride was mixed with a saturated solution (in 0.4 N hydrochloric acid) of iodine labeled with radioactive iodine isotope I^{131}. The iodine concentration in the investigated solution was $8.73 \cdot 10^{-4}$ M, that of iodine chloride was $1.75 \cdot 10^{-3}$ M.

The components of the system were separated, the molecular iodine being extracted with chloroform which substantially does not extract iodine chloride from hydrochloric acid solution; the separating operation took 4-5 minutes. The iodine from the chloroform solution and the iodine chloride from the hydrochloric acid solution

TABLE 1

System I_2-ICl

Experiment number	Activity	
	I_2	ICl
1	386	359
2	380	393
3	835	799
4	872	824
5	1218	1225

TABLE 2

System ICl-KIO_3

Experiment number	Duration of exchange (hours)	Activity	
		ICl	KIO_3
1	37	593	11
2	36	290	0
3	38	340	3

TABLE 3

System ICl-$NaIO_4$

Experiment number	Duration of exchange (in hours)	Activity	
		ICl	$NaIO_4$
1	35	226	2
2	37	317	1

were converted by sodium sulfate into iodide solutions from which silver iodide was precipitated by mixing with equal amounts of silver nitrate solution. The precipitate was filtered and subjected to measurement of activity with the Geiger-Muller counter as described in the handbook of Schweitzer and Whitney [11]. The activity of samples (Tables 1-3) is expressed as the number of impulses per minute.

The results set forth in Table 1 show that exchange between iodine and iodine chloride in 0.4 N hydrochloric acid solution is completed in a period of less than 5 minutes (period of separation).

Iodine chloride was labeled with radioactive iodine in a study of the exchange reactions of iodine chloride with iodate and with periodate.

The concentration of iodine chloride and potassium iodate in the system ICl-KIO_3 was $3.06 \cdot 10^{-2}$ M; the concentration of iodine chloride and sodium periodate in the system ICl-$NaIO_4$ was $7.20 \cdot 10^{-3}$ M.

The components in these systems were fractionated by extraction of the iodine chloride with diethyl ether. After fractionation, the respective compounds of iodine were reduced to iodide and then converted to precipitated silver iodide for measurement of activity.

The results of the experiments presented in Tables 2 and 3 show that exchange of iodine between iodine chloride on the one hand and iodate or periodate on the other hand does not take place in 0.4 N hydrochloric acid solution at 18° after 35-38 hours.

The occurrence of rapid exchange with iodine and with iodine chloride confirms the possibility of formation in solution of the unstable polyiodide $[I(I_2)]Cl$, which leads to iodine exchange:

$$ICl + I^{*}_{2} \rightleftharpoons [I(I^{*}_{2})]Cl = I^{*}Cl + I^{*}I.$$

The absence of exchange between iodine chloride and iodate or periodate indicates that under the experimental conditions there is no reversible chemical reaction between these substances.

SUMMARY

1. Complete exchange occurs in less than 5 minutes in the system I_2-ICl in 0.4 N hydrochloric acid solution at 18°. This phenomenon may be explained by the formation of the unstable polyiodide $[I(I_2)]Cl$.

2. Under the same conditions no exchange occurs after 35-38 hours between ICl on the one hand and KIO_3 or $NaIO_4$ on the other.

LITERATURE CITED

[1] A. I. Brodsky, Chemistry of Isotopes (Academy of Sciences USSR Press, 1952), 219.

[2] R. Dodson and R. Fowler, J. Am. Chem. Soc. 61, 1215 (1939).

[3] Myers and Kennedy, J. Am. Chem. Soc. 72, 897 (1950).

[4] K. B. Zaborenko, M. B. Neiman and V. I. Samsonova, Proc. Acad. Sci. USSR 64, 541 (1949).

[5] M. Cottin and M. Haissinsky, Compt. rend. 224, 1636 (1947).

[6] M. Cottin and M. Haissinsky, J. chim. phys. 48, 500 (1951).

[7] Gmelins Handbuch der anorg. Chem. 8, 463 (1931).

[8] A. Skrabal and F. Buchta, Chem. Ztg. 33, 1193 (1909).

[9] A. I. Gengrinovich, Pharmacy 6, 5 (1946).

[10] R. Lang, Z. anorg. u. allgem. Chem. 142, 235 (1925).

[11] G. K. Schweitzer and I. B. Whitney, Radioactive Tracer Techniques (Foreign Literature Press, 1951), 78.

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HYPOTRIIODIC ACID

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Outstanding among the complex compounds is the extensive class of the polycompounds [1,2], the most typical representatives of which are the polyhalides. The structure of polyhalides, the nature of the coordinative bond, the qualitative and (in part) quantitative calculation of the energy of the coordinative bond are extremely satisfactorily accounted for from the standpoint of polarization concepts. These explanations are extensively used in descriptions of polyhalides in the well-known handbooks [3-5], and also in a series of papers on the chemistry of polyhalides. All the polyhalides studied up to now have the general formula $Me^n [X_n (Y_2)m]$, where the halogen anion X^- is the coordination center, and the addends are molecules of halogen, most frequently the same (X_2) or another (Y_2). On the basis of polarization concepts, we should expect polyhalides to exist with a positive halogen ion as the coordination center.

The discovery of such a polyhalide would be of fairly great interest for two reasons. Firstly, very little is known about cationic poly compounds; secondly, it would confirm that polarization plays a most decisive role in the formation of polyhalides because the cation X^+ must possess marked polarizing properties. The search for polyhalides (derivatives of an electropositive halogen ion) ought to commence with compounds containing the I^+ cation as the coordination center and an iodine molecule as addend. The reason is that of the possible positive univalent halogen cations, the most stable form is provided by iodine, while the iodine molecule possesses the highest polarization.

The absence from the literature of definite data about the existence of a polyhalide with the $[I^+ \ldots I_2]$ cation is evidently to be attributed to the difficulties of experimenting with compounds of univalent electropositive iodine due to the instability of such compounds. The anion of hypoiodous acid is relatively stable only in alkaline solutions of its salts; but in acid and neutral solutions very rapid breakdown takes place to iodine and iodic acid. Iodine chloride, for example, hydrolyzes in aqueous solution, and the resultant hypoiodous acid likewise rapidly breaks down.

A few publications have nevertheless appeared in which reference is made to a substance with the group I_3^+ of interest to us. In the middle of the last century Lensen and Lowental [6] found that oxidation of I^- ions with permanganate followed by removal of the excess of the latter gave a solution in which (to quote their words) "on the basis of analysis the presence can be inferred of a compound I_3O". In modern nomenclature the compound would have the formula I_6O. In modern chemical language we may say that, in the opinion of Lensen and Lowental, they had obtained a solution of the compound HI_3O ($I_6O + H_2O = 2HI_3O$).

Lensen and Lowental used the following analytical procedure in arriving at the above conclusion: Excess KI solution was run into an aliquot portion of the solution, and the separated iodine was back-titrated with $SnCl_2$ solution; a second aliquot portion of the solution was shaken with benzene until the iodine was completely extracted, potassium iodide solution was added to the aqueous layer, and the liberated iodine was again back-titrated with $SnCl_2$ solution. The ratio of the volume of $SnCl_2$ solution consumed in the titration of the first portion of solution to the volume of $SnCl_2$ solution consumed in titration of the second portion was 10:3. The analytical results are consistent with the assumption that the solution under investigation contains a substance with the formula HI_3O, which is the product of addition of iodine to hypoiodous acid: $I_2 + HIO = HI_3O$.

Addition of potassium iodide solution to an aliquot portion of the investigated solution actually results in release of 10 moles iodine per 5 moles:

$$5HI_3O + 5I' + 5H^{\cdot} = 10I_2 + 5H_2O.$$

Extraction of the iodine with benzene is accompanied by breakdown of the HI_3O:

$$5HI_3O = 7I_2 + HIO_3 + 2H_2O.$$

The iodic acid remaining in the aqueous solution loses 3 moles of iodine when potassium iodide is run in:

$$HIO_3 + 5I' + 6H^{\cdot} = 3I_2 + 3H_2O.$$

Interest in the work of Lensen and Lowental was heightened after A. Skrabal [7], in a study of the reaction of iodine with caustic alkalies, established the formation in the system $NaOH-I_2$ of a substance NaI_3O, similar to the compound found by Lensen and Lowental (it must be pointed out that the formation of this substance in the system iodine-caustic alkali had already been suggested by Dusman [8] several years before Skrabal). Skrabal's claims about the formation in this system of the compound NaI_3O were based on indirect evidence derived from the kinetics of the reaction of iodine with caustic alkali. In the same paper Skrabal points out that the compound NaI_3O in its nature must be similar to the polyiodide NaI_3. Skrabal proposed the name "hypotriiodic acid" for the hypothetical acid HI_3O corresponding to the salt.* According to Skrabal, just as HI_3 is formed on addition of iodine to hydriodic acid, so hypotriiodic acid must be the product of addition of iodine to hypoiodous acid, i.e. HI_3O must be regarded as a polyiodide. Skrabal points to the long-standing analogy between halogens and the sulfur group: if polyiodides correspond to polysulfides, then hypotriiodic acid corresponds to thiosulfuric acid $H_2S_2O_3$.

Skrabal and Buchta [9] proposed a method for the preparation of solutions of hypotriiodic acid: 5 ml 0.1 M KI solution, mixed with 250 ml 5 M sulfuric acid and 100 ml saturated (in the cold) solution of manganese sulfate, was oxidized with 32 ml 0.1 N permanganate solution – a fivefold excess on the assumption that hypotriiodic acid is formed according to the equation:

$$30KI + 8KMnO_4 + 27H_2SO_4 = 10HI_3O + 19K_2SO_4 + 8MnSO_4 + 22H_2O.$$

After standing for 17 hours, the excess of permanganate was reduced with 20 ml 0.2 N oxalic acid. In a variant of the procedure, 70 ml permanganate solution was added and the excess immediately reduced with oxalic acid.

Skrabal and Buchta analyzed the solution in a similar manner to Lensen and Lowental, but they titrated the iodine with sodium thiosulfate solution and extracted the iodine with chloroform. In the analysis they determined firstly the volume of thiosulfate solution (A) consumed in titration of the iodine released when potassium iodide was added to an aliquot of the solution under investigation; secondly they determined the volume of thiosulfate solution (C) consumed in titration of the iodine released when potassium iodide was added to the solution remaining after extraction of the iodine. The A/C ratio was 10:3, and this (as mentioned above) leads to the formula HI_3O.

In the same paper the authors put forward the hypothesis that addition of iodine stabilizes the hypoiodous acid and that the presence of ions of divalent manganese as one of the reaction components is essential. Skrabal and Buchta draw attention to the following experimental observation: Although chloroform extracts iodine when shaken with the investigated solution, the latter does not give the starch-iodide reaction; in their opinion this confirms that all the molecular iodine adds on to hypoiodous acid.

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* We shall make use of the formula HI_3O and the name "hypotriiodic acid" in the course of this paper, although it would of course be more correct to write the formula of this substance in acid solutions as I_3OH and to describe it not as an acid but as a base due to the predominance in IOH of a basic type of dissociation.

EXPERIMENTAL

Our experiments confirmed the correctness of the method of preparation of hypotriiodic acid described by Skrabal and Buchta. We are bound to comment, however, that the results solely of chemical analysis do not provide conclusive evidence of the existence of the compound HI_3O in solution. It could also be suggested that the solution could contain free iodine and iodic acid in the ratio to give A : C = 10:3 on analysis. Actually the ratios of substances according to the experimental procedure are in some degree fortuitous. Although the fall in concentration of manganese sulfate increases the value of C, as follows from the experiments of Skrabal and Buchta, by decreasing the duration of standing of the solution with excess of permanganate we can find an instant at which A : C will be equal to 10:3. The same may be said about the increase in concentration of permanganate. We carried out special experiments whose results are presented in Table 1. These show that the content of electropositive iodine * in solution increases continuously with time, so that it is impossible to speak of the formation of a definite compound at any given instant.

TABLE 1

Duration of standing with excess permanganate (in hours)	Ratio A : C
0.085	10 : 0
1	10 : 1.85
25.5	10 : 4.4
50	10 : 5.5
72	10 : 6.2
94.5	10 : 6.4
118	10 : 6.4

Even the absence of the starch-iodide reaction, which Skrabal and Buchta regarded as one of the main proofs of the existence of hypotriiodic acid in solution, is not convincing because molecular iodine of course only gives the starch iodide reaction in presence of iodine anions whose presence in the solution in question is excluded for obvious reasons. Consequently an unequivocal answer to the question whether the solution under consideration contains hypotriiodic acid or the equivalent mixture of iodine and iodic acid cannot be given on the bases of the experimental data of Skrabal and Buchta.

On repeating the experiments of these authors, we obtained only one piece of evidence (and that only indirect) of the presence of I^+ ions in solution, namely: the electropositive iodine of the solution in question gradually disappears after reduction of the permanganate with oxalic acid, evidently oxidizing the excess of the latter. A control experiment showed that iodate, dissolved in sulfuric acid of the same concentration as that used by Skrabal and Buchta, does not oxidize oxalic acid.

It follows from what has been said that further proof should be sought for the existence of hypotriiodic acid.

Such proofs might be obtained by a study of ionic transfer in Skrabal and Buchta's solution. Such a study in the present case, however, would be impossible for the following reasons: 1) the solution contains a large amount of manganese sulfate, and passage of a current into the anolyte would result, in the very first seconds, in the liberation of manganese dioxide which would undoubtedly interfere with quantitative examination of the anolyte; 2) hydrogen is released at the cathode and would prevent quantitative investigation of the catholyte since the electropositive iodine at the cathode would be reduced; 3) ionic transfer must be effected in a solution free from excess of permanganate, and such a solution is (as already mentioned) extremely unstable because the electropositive iodine therein is fairly quickly reduced.

As was noted above, the data of Skrabal and Buchta permit the conclusion that not only HI_3O but also systems with I_2 and HIO_3 are formed. The most convincing proof of the presence in the solution in question of hypotriiodic acid would therefore be the detection in the solution of iodine compounds in the $^{+}1$ valence state. Reaction of qualitative analysis are inapplicable to this problem due to the low concentration of iodine and the strong acidity of the solution; it was therefore decided to study with the help of radioactive iodine the exchange between molecular iodine and the electropositive iodine of Skrabal and Buchta's solution, and also the exchange between molecular iodine and iodate. The character of the exchange in these systems ought to indicate whether we are dealing with hypotriiodic acid or with a mixture of iodine and iodic acid.

Exchange of molecular iodine with iodate has been studied by several authors. Hull et al. [10] studied the exchange of iodine with iodate in a sulfuric acid medium. He found that iodine and iodate, dissolved in 1 N sulfuric acid, do not exchange in appreciable amounts after 1-2 minutes. 10-15% exchange was found after the same period when iodine and iodate were dissolved in 20 N hot sulfuric acid. Myers and Kennedy made a detailed kinetic study [11] of iodine/iodate exchange in a medium of perchloric acid. They found that the velocity of

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* By the term electropositive iodine we refer here (and later) to iodine in the 1^+ and 5^+ (HIO_3) stages of oxidation.

TABLE 2

Iodine / Iodate Exchange in SN H_2SO_4.

Period of exchange (in hours)	Activity (in signals / min.)		Percent exchange
	of iodate	of iodine	
0	1	580	0
26.5	36	495	7.26
50.5	48	560	8.58
96	74	569	13.0
122.5	88	587	15.0
140.5	99	524	18.9
172.5	85	414	20.6
194.5	74	327	22.7
233	82	303	27.0
289.5	90	283	31.8

TABLE 3

Exchange Between Molecular and Electropositive Iodine of the Investigated Solution

Activity of molecular iodine	Activity of electropositive iodine	Ratio of activity of molecular iodine to activity of electropositive iodine
317	32	10
754	62	12
272	22	12

exchange was small and depended in great measure upon the concentration of the components of the system and upon the acidity of the solution. Cottin and Haissinsky [12] dissolved 50 mg each of iodate and radioactive iodine in 500 ml 0.5 N acetic acid and distilled off the iodine, after 40-hours standing at room temperature, by boiling the solution for 35 minutes. Under these conditions they found complete exchange of iodine with iodate.

We were interested in exchange of iodine with iodate in a sulfuric acid medium. Only one of the cited paper [10] relates to this sytem, and the data could not satisfy us, firstly because the authors used a short-lived radioactive iodine isotope with a half-life period of 25 minutes which prevented study of the exchange over a more or less long period, and secondly because the exchange was only studied qualitatively. We therefore decided to study the iodine/ iodate exchange in sulfuric acid solution in which the concentrations of iodine, iodate and sulfuric acid were close to the possible concentrations of these substances in the hypotriiodic acid solution that we were investigating.

We studied the iodine/ iodate exchange at 18° in 5 N sulfuric acid. The mean concentrations of iodine and iodate in different experiments were respectively $6 \cdot 10^{-4}$ and $1.2 \cdot 10^{-3}$ M.

In all experiments molecular iodine was labeled with radioactive iodine (I^{131}). The components of the system under investigation were separated by extraction of the molecular iodine with chloroform. The iodine from the chloroform solution and the iodate from the aqueous solution were then converted into precipitates of silver iodide which were filtered off and prepared for measurement of activity with the Geiger-Muller counter [13].

Results of one of the experiments are set forth in Table 2. Slow exchange between iodine and iodate was found under the experimental conditions: the period of half exchange, found by extrapolation, was 460 hours; the velocity of iodine/ iodate exchange was of the order of 10^{-6} mole/ liter hour.

Since the solution of Skrabal and Buchta contains a considerable amount of manganese sulfate, we ran a control experiment on iodine/ iodate exchange in a sulfuric acid solution of manganese sulfate of the same concentration as in the solution of Skrabal and Buchta. It was established that ions of divalent manganese do not influence the velocity of exchange.

We carried out the exchange of molecular iodine with the iodine compounds of Skrabal and Buchta's solution in the following manner: to the solution, prepared as described above, after reduction of the excess of permanganate, was added a few drops of solution of radioactive molecular iodine without a carrier. After stirring thoroughly for a few seconds, extraction of the iodine with chloroform was started. The duration of extraction was 4-5 minutes. The iodine from the chloroform solution and the iodic acid from the aqueous layer were converted into solutions of iodide, each of which was "diluted" with 15 ml 0.1 N potassium iodide and converted into silver iodide precipitate.

What results of measurement of activity of the samples should have been obtained if the investigated solution were really a solution of hypotriiodic acid? Of the three iodine atoms entering into the composition of each molecule of hypotriiodic acid $HIO \cdot I_2$, at least two (i.e. the coordinated iodine molecule) should exchange very quickly with molecular radioactive iodine introduced for exchange. Let us assume that the third atom likewise exchanges very quickly with molecular iodine. Such an assumption is perfectly plausible because, as previously shown [14], iodine chloride ICl, which contains the I^+ cation, very quickly exchanges in hydrochloric acid solution with molecular iodine. In this case the molecular iodine and the electropositive iodine in the investigated solution must possess identical specific activities. As can be easily calculated, this is reflected in the results of measurements of radioactivity by a value of 10.9 for the ratio of the activity of a sample corresponding to the coordinate molecule of iodine in hypotriiodic acid to the activity of the sample corresponding to univalent electropositive iodine of the same compound (in the calculation we neglect the amount of iodine introduced for exchange since the latter has no carrier, i.e. its amount is negligible).

Results of experiments on the exchange of molecular iodine with electropositive iodine of Skrabal and Buchta's solution are presented in Table 3.

As we see from Table 3, the molecular iodine in the investigated solution completely exchanges in 4-5 minutes with the electropositive iodine of this solution; the picture is precisely the reverse of that in the system iodine iodate in which over the same period not even a trace of exchange was observed.

Thus, the experiment fully confirms the claim of Skrabal and Buchta that oxidation of iodide with excess of permanganate in an acid medium in presence of a large amount of manganese sulfate leads to formation of hypotriiodic acid HI_3O. The compound is named more correctly triiodine-hydroxide.

On the basis of comparison of the results of the above experiments with our earlier results [14] (rapid exchange of iodine chloride with molecular iodine), we may conclude that univalent electropositive iodine is undoubtedly capable of forming complexes and in particular polyiodides.

SUMMARY

1. Exchange between iodine and iodate in 5 N sulfuric acid was studied with iodine and iodate concentrations of respectively $6 \cdot 10^{-4}$ and $1.2 \cdot 10^{-3}$ M. Slow exchange (period of half exchange 460 hours) was found under the experimental conditions.

2. Under similar conditions complete exchange was found in a period of less than 5 minutes between the molecular and the electropositive iodine of Skrabal and Buchta's solution.

3. On the basis of the different picture of exchange in the two cases in question, it is concluded that the electropositive iodine in the solution has a valence of +1 and that, consequently, Skrabal and Buchta actually obtained hypotriiodic acid – a polyiodide with a I^+ cation as the center of coordination and a molecular of iodine as the addend.

LITERATURE CITED

[1] Ya. A. Fialkov, J. Gen. Chem. 18, 147 (1948).

[2] B. F. Ormont, Structure of Inorganic Compounds (1950).

[3] B. V. Nekrasov, Course of General Chemistry (1952), 823.

[4] A. A. Grinberg, Introduction to the Chemistry of Complex Compounds (1951), 266.

[5] Van Arkel and De-Boer, The Chemical Bond (1935), 139.

[6] E. Lensen and I. Lowental, J. prakt. Chem. 86, 219 (1862) (Cited in [7]).

[7] A. Skrabal, Monatsh. 28, 319 (1907).

[8] S. Dusman, J. Phys. Chem. 8, 453 (1904); Chem. Zentr. 1904, 1489.

[9] A. Skrabal and F. Buchta, Chem. Ztg. 33, 1193 (1907).

[10] D. E. Hull, C. H. Shiflett and S. C. Lind, J. Am. Chem. Soc. 58, 535 (1936).

[11] Myers and Kennedy, J. Am. Chem. Soc. 72, 897 (1950);

[12] M. Cottin and M. Haissinsky, Compt. rend. 224, 1636 (1947).

[13] G. K. Schweitzer and I. B. Whitney, Radioactive Tracer Techniques (1951), 78.

[14] V. L. Pavlov and Yu. Ya. Fialkov, J. Gen. Chem. 26, 1531 (1956) (T.p. 1711).*

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THE PROBLEM OF THE ANODIC PRECIPITATES OBTAINED DURING THE ELECTROLYSIS OF SILVER SALTS. II.

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Preparation of an anodic percipitate from solutions of silver sulfate is associated with considerable difficulties due to the low solubility of the sulfate in water. The electrolyte contains a relatively small number of silver ions; separation of the precipitate at the anode is accompanied by release of gases, which is particularly marked after the electrolysis has proceeded for some time. For this reason the application of high current densities is not possible. It is necessary, when electrolyzing large amounts of electrolyte, to use mechanically stirred solutions and a relatively low current density.

We performed the electrolysis of a saturated solution of silver sulfate in a large electrolyzer with a capacity of 2-2.5 liters, with stirring and cooling to 2-3°, and with application of a current density of 0.010-0.015 A/cm^2. The electrodes were platinum plates each with an area of 4 cm^2.

Under these conditions it was possible to form an anodic precipitate in 5-6 hours without simultaneous release of gases. The use of diaphragms, neutralization of the solution and later saturation, as proposed by Mulder [1], proved superfluous. No solution of the anodic precipitate in the sulfuric acid formed was observed in our experiments, due to the very low acid concentration at the anode. Crystals that separated from the electrodes collected in flat glass vessels standing below them.

Well-formed crystals are formed under these conditions at the anode, although not as large as in the case of electrolysis of other silver salts [2]. The precipitates had a black color and a metallic luster. In structure and character of growth (see diagrams) they are very similar to the crystals of anodic precipitate obtained from solutions of silver fluoride, and consist of regularly formed or distorted octahedra. Debyeograms of the crystals showed that they belong to the cubic system and have a cubic face-centered lattice with a constant of 9.90 A. The crystals are fairly stable. Their composition remains nearly unchanged even after 1-2 months when kept in the dark and in a cool place. The crystals were analyzed after drying in a desiccator over phosphorus pentoxide to constant weight. Data for the detailed analysis of the precipitate are given in table. Having established the ratio Ag_a/Ag_c, which had a mean value of 0.62, we could immediately conclude that the formula $5\ Ag_2O_3 \cdot 2Ag_2SO_4$ proposed by Tanatar [3] for the anodic precipitate obtained from silver sulfate is inaccurate. The ratio $Ag_a/$ $/Ag_c$ would have been 0.7 if this formula had been correct. Results of analysis of the precipitate also showed that Tanatar gave the wrong formula. A detailed study of the precipitate showed that the empirical formula proposed by Mulder [1] is substantially correct – $Ag_{14}S_2O_{24}$ ($5\ Ag_2O_2 \cdot 2Ag_2SO_7$). This is supported by the following proposed reactions. Heating to 1000° gives

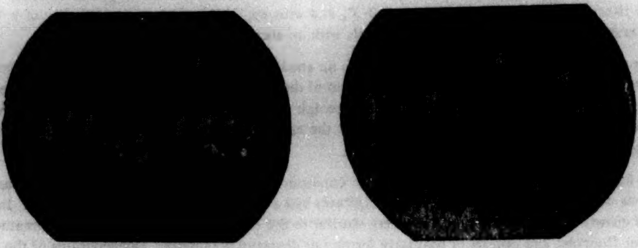
$$5Ag_2O_2\ \ 2Ag_2SO_7 = 10Ag \cdot 2Ag_2SO_4 + 16O.$$

Heating at 125-130° gives

$$5Ag_2O_2 \cdot 2Ag_2SO_7 = 5Ag_2O \cdot 2Ag_2SO_4 + 11O.$$

TABLE 1

Value determined	Found (weight %)	Calculated from formula (weight %)
Total amount of silver	77.04	77.12
Amount of oxygen released at 125-130°	8.22	8.99
Amount of oxygen released on heating to 1000°	13.08	13.07
Amount of sulfate ion	10.12	9.81
Amount of silver washed out by hot water	22.01	22.03
Amount of silver in the residue after treatment with hot water	54.85	55.09
Amount of oxygen released on boiling with water	4.71	4.90
Ag_a/Ag_c	0.619	0.636



Crystals of anodic silver precipitate (× 200).

Treatment with hot water gives

$$5Ag_2O_2 \cdot 2Ag_2SO_7 = 5Ag_2O_2 + 2Ag_2SO_4 + 6O.$$

Hot water very easily decomposes the precipitate with vigorous liberation of oxygen, thus demonstrating the instability of Ag_2SO_7, for Ag_2O_2 is not decomposed by hot water.

Mulder's conclusions that the salt $2Ag_2SO_7$ is a derivative of a tetrabasic acid $H_4S_2O_{14}$ containing hepta- and pentavalent sulfur are incorrect. Some light is thrown upon the structure of the precipitate and the structure of other anodic precipitates by our proposed method of establishing the ratio between the amount of silver entering into the composition of the anodic precipitate (Ag_a) and the amount of silver released after the same period at the cathode (Ag_c) [2].

As mentioned above, this ratio has a mean value of 0.62. Since the empirical formula of the precipitate contains 14 silver atoms, $Ag_c = 14/0.62 \approx 22$. Thus at the cathode the reaction is $22\ Ag^+ + 22e^- = 22Ag^0$, i.e. 22 electrons are released in formation of $5Ag_2O_2 \cdot 2Ag_2SO_7$ at the anode and the value of Ag_a/Ag_c must be $14/22 = 0.636$. If we assume that Ag_2SO_7 is a trivalent silver salt of monopersulfuric acid in its ortho form $H_2SO_5 \cdot 2H_2O=$

$= H_6SO_7$, then formation of $2Ag_2SO_7$ involves release of 12 electrons, and that of $5Ag_2O_2$ involves release of 10 electrons – total of 22 electrons.

The reaction with oxalic acid was also of interest. Oxidation with oxalic acid of the anodic precipitates obtained from silver nitrate, fluoride and perchlorate [2] gave constant results; this was not observed, however, in the case of the sulfate precipitate, although the results were always higher than would correspond to 6 active oxygen atoms. The reason is that in the oxidation with oxalic acid $2Ag_2SO_7$ releases 6 oxygen atoms and changes into $2Ag_2SO_4$, while Ag_2O_2 does not give consistent results in reaction with oxalic acid [4].

A final solution of the problem of the structure of the anodic precipitate ($5Ag_2O_2 \cdot 2Ag_2SO_7$) has not been obtained.

SUMMARY

1. Electrolysis of aqueous solutions of silver sulfate leads to formation at the platinum anode of crystalline precipitates with a metallic luster which are stable at the ordinary temperature.

2. Detailed chemical analysis and the application of our proposed method of establishing the ratio of the amount of silver entering into the composition of the anodic precipitate to the amount of silver precipitated during the same period at the cathode enabled us to assign the formula $5Ag_2^{II}O_2 \cdot 2Ag_2^{III}SO_7$ to the precipitate.

3. The crystals of the precipitate belong to the cubic system and have a face-centered lattice with the constant 9.90 A.

4. The composition of the precipitate is always the same, irrespective of the conditions of preparation, if no gases are simultaneously evolved at the anode.

LITERATURE CITED

[1] E. Mulder, Rec. trav. chim. 18, 91 (1899); 19, 115, 165 (1900); 22, 401 (1903).

[2] M. S. Skanavi-Grigoryeva and I. L. Shimanovich, J. Gen. Chem. 24, 1490 (1954)(T. p. 1475)*

[3] S. Tanatar, Z. anorg. Chem. 28, 331 (1901).

[4] E. Jirsa, Z. anorg. u. allgem. Chem. 158, 33 (1925).

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INFLUENCE OF VARIOUS ELEMENTS ON THE SOLUBILITY OF CARBON CARBON IN MOLTEN IRON

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The influence of phosphorus, chromium, manganese, sulfur and vanadium on the solubility of carbon in molten iron is considered in the present communication. A study is also made of the effect of silicon upon the solubility of carbon in manganese and ferrochrome. Some of the elements increase the solubility of carbon, while others diminish it. The difference in effect is bound up with the difference in free energy of interaction of the elements of the alloy.

A carbon resistance furnace was used for the experiments.

Starting materials were: 1) iron-carbon alloy (4.0-4.5% C, 0.1-0.15% Si, 0.08-0.1% Mn, 0.03% S, 0.06-0.07% Cr, 0.007% P); 2) ferrophosphorus (24% P, 0.2% C, 0.017% S, 0.12% Cr, 0.14% Mn and 0.4% Si); 3) chromium (99.1% Cr, 0.54% Fe, 0.2% Si, 0.15% Al, 0.05% C; 4) iron sulfide (35% S, 0.1% Si, 0.2% Mn, 0.15% C); 5) ferromanganese (92% Mn, 0.88% C); 6) electrolytic manganese (99.9% Mn); 7) ferrovanadium (approx. 38% V); 8) technical silicon (approx. 97% Si).

The starting substances were charged in the required amounts into a graphite crucible and covered at the top with a thick layer of wood charcoal. The melt was periodically stirred with a graphite rod and held in the furnace for 40-60 minutes. It was then poured into a massive iron mould and samples were taken for chemical analysis after solidification. The results obtained are presented in Tables 1 and 2 (see also [1-4]).

The data obtained for the solubility of carbon in iron-sulfur melts as well as for the miscibility region are in good agreement with the results of other authors [5, 6]. They are lower, however, by about 0.5% than the values obtained by Turkdogan et al.[7, 8] in a nitrogen atmosphere for the systems Fe-S-C and Fe-P-C. The latter authors also observe that the difference (ΔN_C^X) between the atom fraction of carbon (N_C) in the carbon-saturated ternary alloy Fe-X-C and the fraction (N_C^C) in the case of the binary Fe-C alloy is substantially independent of the temperature and is a linear function of the atomic fraction of the third element (N_X):

$$\Delta N_C^X = N_C - N_C^C = aN_X. \tag{1}$$

Equation (1) is valid for not too high values of N_X. Its applicability to our data was tested by calculation of the solubility of carbon in the binary Fe-C alloy. For this purpose the following formula [7] was used:

$$\log N_C^C = -\frac{560}{T} - 0.375. \tag{2}$$

It should be noted that in our experiments under-saturation with carbon apparently occurred. Calculation of N_C^C according to Formula (2) gives higher values than the values of N_C found by us with low contents of the third element (Mn, Cr).

For this reason the solubility of carbon in iron and manganese (N_C^C) at 1450° was assumed to be approximately 0.19.

TABLE 1

Solubility of Carbon in Fe-P, Fe-Cr, Fe-Mn and Fe-V Melts at a Temperature of 1450° and in Fe-S Melts at 1250°

Fe–P–C alloys				Fe–Cr–C alloys			
weight %		atom fractions		weight %		atom fractions	
P	C	P	C	Cr	C	Cr	C
1.5	4.0	0.023	0.161	1.08	4.75	0.010	0.190
1.9	3.4	0.030	0.139	2.08	4.85	0.019	1.192
3.17	3.34	0.049	0.136	3.92	5.10	0.035	0.200
4.50	2.90	0.071	0.118	6.23	5.35	0.056	0.208
6.0	2.50	0.095	0.102	9.51	5.55	0.085	0.214
12.0	1.17	0.190	0.048	11.24	5.70	0.099	0.218
13.6	0.48	0.218	0.020	13.06	5.80	0.115	0.221
19.1	0.21	0.297	0 008	15.14	5.95	0.133	0.226
21.0	0.21	0.323	~0.008	20.5	6.25	0.177	0.236
23	0.20	0.338	~0.008	23.0	6.40	0.198	0.238
				27.5	6.70	0.234	0.247

Fe–Mn–C alloys				Fe–V–C alloys			
Mn	C	Mn	C	V	C	V	C
1.4	4.75	0.012	0.19	1.0	5.1	0.009	0.200
2.2	4.80	0.019	0.191	2.1	5.3	0.021	0.207
4.2	4.9	0.036	0.194	5.0	5.8	0.045	0.221
8.6	5.1	0.074	0.20	7.0	5.8	0.060	0.222
18.3	5.4	0.155	0.21	16.7	6.47	0.146	0.241
33.8	5.9	0.281	0.226				
43.0	6.2	0.354	0.234				
66.1	6.5	0.538	0.243				
76.5	6.7	0.618	0.249				

Fe–S–C alloys			
S	C	S	C
0.048	4.4	0.0007	0.177
0.06	4.4	0.0009	0.177
0.14	4.2	0.0021	0.170
0.31	4.0	0.0047	0.162
0.71	3.3	0.0111	0.137

As we see from Fig. 1, the agreement in the case of Fe-Mn-C alloys is quite good. Our data (the straight line 1) are consistent with the equation:

$$\Delta N_{\mathrm{C}}^{\mathrm{Mn}} = 0.13 N_{\mathrm{Mn}}, \tag{3}$$

On the other hand the values of Turkdogan et al.[7] (straight line 1') are in accord with the equation

$$\Delta N_{\mathrm{C}}^{\mathrm{Mn}} = 0.1 N_{\mathrm{Mn}}. \tag{4}$$

It also follows from Fig. 1 that the starting points for the ternary alloy Fe-Cr-C (straight line 2) are adequately represented by

$$\Delta N_C^{Cr} = 0.3 N_{Cr},\qquad (5)$$

TABLE 2

Solubility of Carbon in Si-Mn and Fe-Cr-Si Alloys at 1450°

Si–Mn–C alloys				Fe–Si–Cr–C alloys			
weight %		atom fractions		weight %		atom fractions	
Si	C	Si	C	Si	C	Si	C
9.5	3.15	0.155	0.12	3.0	6.0	0.047	0.222
14.2	2.70	0.226	0.10	17.7	2.6	0.267	0.093
20.0	1.45	0.316	0.053	19.6	2.4	0.298	0.085
23.7	1.02	0.368	0.037	24.5	1.5	0.367	0.053
28.5	0.3	0.436	0.011	27.3	0.8	0.411	0.028
35.0	0.1	0.512	0.003	35.3	0.5	0.504	0.017
40.0	0.1	0.565	0.003	41.7	0.3	0.575	0.010
42.8	0.1	0.594	0.003	47.5	0.1	0.634	0.003
				57.0	~0.1	0.716	~0.003
				60.0	~0.1	0.738	~0.003

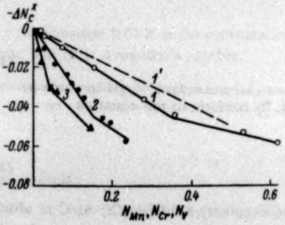

Fig. 1. Relation between $-\Delta N_C^X$ and the concentration of alloying element N_X. 1) For iron-manganese-carbon alloys, 1') the same according to the data of [7], 2) for iron-chromium-carbon alloys, 3) for iron-vanadium-carbon alloys.

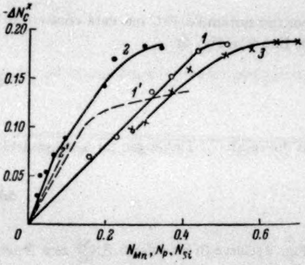

Fig. 2 . Relation between $-\Delta N_C^X$ and the concentration of alloying element N_X. 1) For manganese-silicon-carbon alloys, 1') for iron-silicon-carbon alloys (according to the data of [7]), 2) for iron-phosphorus-carbon alloys, 2') ditto according to the data of [7], 3) for (iron + chromium)-silicon-carbon alloys.

while for the system Fe-V-C the following expression is approximately valid (see straight line 3):

$$\Delta N_C^V = 0.75 N_V.\qquad (6)$$

It is interesting to note that silicon displaces carbon less easily in Mn-Si-C alloys (see straight line 1, Fig. 2):

$$\Delta N_C^{Si} = -0.41 N_{Si},\qquad (7)$$

than in the system Fe-Si-C [7] (see straight line 1', Fig. 2):

$$\Delta N_{C}^{Si} = -0.71 N_{Si}. \tag{8}$$

The dependence of ΔN_{C}^{S} in Fe-S-C melts is expressed in our case by the equation

$$\Delta N_{C}^{S} = -4.0 N_{S}, \tag{9}$$

the numerical coefficient of which is four times larger (Fig. 3) than that obtained by Turkdogan et al.[8].

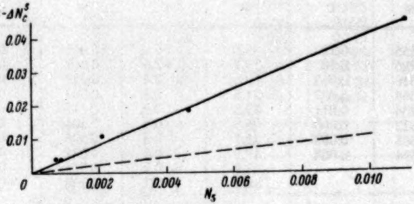

Fig. 3. Relation between $-\Delta N_{C}^{X}$ and the sulfur concentration in iron-sulfur-carbon alloy (broken plot according to data of [8]).

For the system Fe-P-C our data conform to the following expression within the limits of $0.075 \geq N_P \geq 0$ (straight line 2 in Fig. 2)

$$\Delta N_{C}^{P} = -N_{P}, \tag{10}$$

whereas the results of Turkdogan for $0 \leq N_P \leq 0.045$ (straight line 2', Fig. 2) conform to the equation

$$\Delta N_{C}^{P} = -0.84 N_{P}. \tag{11}$$

Fig. 2 (Curve 3) also shows ΔN_{C}^{Si} as a function of N_{Si} for the pseudoternary alloy (Fe,Cr)-Si-C in which the percent ratio of Fe to Cr is close to unity. In spite of the observed scatter of the data, probably due to the absence of special precautions in our experiments (inert atmosphere, withdrawal of samples at intervals and their rapid cooling), Equation (1) was valid, at least for small values of N_X. Since the activity of graphite at the given pressure and temperature is a perfectly definite magnitude, we have for alloys saturated with carbon:

$$a_{C} = N_{C}\gamma_{C} = a_{C}^{C} = N_{C}^{C}\gamma_{C}^{C}, \tag{12}$$

from which it follows that the dependence of

$$\Delta N_{C}^{X} = N_{C} - N_{C}^{C} = N_{C}^{C}\left(\frac{\gamma_{C}^{C}}{\gamma_{C}} - 1\right) \tag{13}$$

on the composition of the ternary alloy is governed only by the effect of the third element on the activity coefficient of the carbon. In other words, the magnitude of ΔN_{C}^{X} permits evaluation of the deviation of γ_C from γ_C^C. We may thus write the following generalized expression which is applicable to all dissolved elements:

$$\Delta N_Y^X = N_Y - N_Y^Y = N_Y^Y\left(\frac{\gamma_Y^Y}{\gamma_Y} - 1\right). \tag{14}$$

If element X causes an increase in solubility of substance Y (i.e. if $\Delta N_Y^X > 0$), then it lowers the value of γ_Y, making it less than γ_Y^Y, and vice versa.

The influence of the third element X on the coefficient of activity of substance Y in the absence of saturation has been considered in a paper by Pearson and Turkdogan [9]. They point out that the more negative is the value of the isothermal isobaric potential (ΔZ_{YX}) of formation of a compound from the elements X and Y, the stronger is the mutal lowering of their coefficients of activity. Conversely, with positive values of ΔZ_{YX} the coefficients of activity of the dissolved elements become higher than in binary alloys. From this, however, it is impossible to draw the conclusion that the whole of the mutual lowering of the values of γ_X and γ_Y is due to the formation of chemical compounds in the ternary alloy, especially if the compounds are complex and not structurally compatible with the solvent [10].

We shall apply the theory of regular solutions to the clarification of the energetic relationships here found. Although this theory can scarcely be regarded as a quantitative law in the systems concerned, it is nevertheless quite suitable for qualitative conclusions.

For a ternary alloy Me-X-Y:

$$RT \ln \gamma_Y = B_{MeY}N_{Me} + B_{YX}N_X - B_{MeY}N_{Me}N_Y - B_{YX}N_YN_X - B_{MeX}N_{Me}N_X, \tag{15}$$

where N_i are the atom fractions and

$$B_{ij} = ZN'\left(\frac{1}{2}\varepsilon_{ii} + \frac{1}{2}\varepsilon_{jj} - \varepsilon_{ij}\right). \tag{16}$$

In Equation (16) Z is the coordination number, E is the energy of interaction of the two corresponding atoms, and N' is Avogadro's number.

In place of N_Y in Expression (15) we put

$$N_Y = 1 - N_{Me} - N_X, \tag{17}$$

and therefore

$$RT \ln \gamma_Y = B_{MeY}N_{Me}^2 + (B_{MeY} + B_{YX} - B_{MeX})N_{Me}N_X + B_{YX}N_X^2. \tag{18}$$

It follows therefore that for dilute solutions of X and Y in Me, when $N_X^2 \ll N_XN_{Me}$, the activity coefficient of one of the added substances (Y) will decrease with increasing concentration of the other (X) only when

$$B_{MeY} + B_{YX} - B_{MeX} < 0, \tag{19}$$

or, taking Equation (16) into consideration, when

$$\varepsilon_{YX} > \varepsilon_{MeX} + \varepsilon_{YY} - \varepsilon_{MeY}. \tag{20}$$

In the simplest case, when ϵ_{YY} is approximately equal to ϵ_{MeY} (for example ϵ_{CC} and ϵ_{FeC}), this condition leads to the inequality:

$$\varepsilon_{YX} > \varepsilon_{MeX}. \tag{21}$$

In other words, if the energy of interaction between atoms of X and Y is greater than between X and Me, then the introduction of substance X lowers the activity coefficient of substance Y. According to Expression (14), this also signifies that rise of the concentration of X increases the solubility of Y in Me. The Relation (21) holds for X = Mn, Cr and V if Me = Fe and Y = C; under these conditions the solubility of carbon also increases with introduction of Mn, Cr and V. The inequality which is the reverse of (19) resolves itself in the simplest case into the expression

$$\varepsilon_{MeX} > \varepsilon_{YX}, \tag{22}$$

which is valid for X = Si, S and P; Me = Fe; Y = C. Here the solubility of carbon in iron falls with rising concentration of Si, S and P.

Concerning the observed linear relation between ΔN_C^X and N_X, this follows from the simultaneous solution of Equations (14), (18) and (23):

$$\ln \gamma_Y^Y = B'_{MeY} N'^2_{Me}, \tag{23}$$

the last of which relates to the binary Fe-C alloy. Neglecting the term in N_X^2 and limiting ourselves to the first two components of the series obtained by resolution of the exponent of the ratio γ_Y^Y/γ_Y, we find:

$$\Delta N_C^X = \frac{N_C^C}{RT}\left[B'_{FeC}N'^2_{Fe} - B_{FeC}N^2_{Fe} - (B_{FeC} + B_{CX} - B_{FeX})\,N_{Fe}N_X\right]. \tag{24}$$

Equation (24) not only indicates the possibility of a linear relation between the solubility of carbon and the concentration of alloying element, but also accounts for the slight dependence of the slope of the straight line plot of ΔN_C^X versus N_X on the temperature. The value of N_C^C increases with the temperature and this compensates in some measure for the rise of RT. But the factor in the bracket, according to the theory of regular melts, does not depend on the temperature. The data show that the regularities observed in the experiments can be qualitatively clarified with the help of the theory of regular melts.

SUMMARY

1. A study is made of the influence of phosphorus, chromium, manganese, sulfur and vanadium on the solubility of carbon in molten iron, and also of the influence of silicon on the solubility of carbon in fused manganese and ferrochrome.

2. It is shown that the observed regularities of the influence of the nature of the additive and its concentration, as well as of the temperature, can be qualitatively clarified with the help of the theory of regular melts.

LITERATURE CITED

[1] O. A. Esin, L. K. Gavrilov and N. A. Vatolin, Proc. Acad. Sci. USSR 85, 87 (1952).

[2] O. A. Esin and N. A. Vatolin, Bull. Acad. Sci. USSR, Div. Tech. Sci. 1953, 1137.

[3] N. A. Vatolin and O. A. Esin, J. Gen. Chem. 24, 795 (1954)(T.p. 797).*

[4] O. A. Esin and N. A. Vatolin, J. Appl. Chem. 27, 1252 (1954) (T.p. 1187).*

[5] D. A. Spratt and J. A. Kitchener, J. Iron Steel Inst. 172, 383 (1952).

[6] R. Oberhoffer, Technical Iron (Metallurgical Press, 1940), 93.

[7] E. T. Turkdogan and L. E. Leake, J. Iron. Steel Inst. 179, 39 (1955).

[8] E. T. Turkdogan and R. A. Hancock, J. Iron Steel Inst. 179, 155 (1955).

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* T.p. = C.B. Translation pagination.

[9] J. Pearson and E. T. Turkdogan, Problems of Modern Metallurgy 1954, No. 6 (18), 53.

[10] N. N. Levenets and A. M. Samarin, Proc. Acad. Sci. USSR 101, 1089 (1955).

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THE SOLUBILITY OF PERCHLORATES OF ELEMENTS OF THE SECOND GROUP OF THE PERIODIC SYSTEM

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The specific properties of the ClO_4^- ion result in a certain simplification of processes taking place in perchlorate solutions. Interest is therefore attached to a study of the solution and solubility of perchlorates of various metals.

Although a relatively large number of perchlorates have been studied, not much systematic work has been carried out. Only the perchlorates of elements of the 1st group and of the main subgroup of the 2nd group have been studied at all extensively (solubility in water and a number of organic solvents at 25° [1]). The temperature dependence of the solubility has been completely studied only for perchlorates of elements of the 1st group (Na [2], Li [3], K [4-6], Rb and Cs [4, 6]). Data for the solubility of perchlorates of elements of other groups of the periodic system are incomplete and therefore not easily comparable. Reference is made in the literature to the solubility and the temperature dependence of the solubility of perchlorates of Ba, Tl [4], di- and trivalent iron [7], univalent mercury [8], etc., the solubility of perchlorates of Ag [9], Pb [10], and Be [11], etc. A number of the solubilities need to be redetermined more accurately. For example, the solubility of the perchlorates of Cu, Cd, Co, Mn and Ni was determined by adding water to a weighed sample of the salt until the latter had completely dissolved at room temperature [12].

The objective of the present work was the study of the solubility of perchlorates of elements of the 2nd group of the periodic system in water in the 0 to 50° temperature range and a comparison of the solubility of perchlorates of elements of the same group.

Perchlorates of Mg, Ca, Sr, Zn, Cd and Hg were prepared by saturating perchloric acid with the oxides of the corresponding metals (analytically pure grades), and carrying out 2-3 recrystallizations from solution. Be perchlorate was prepared by dissolving beryllium carbonate ("pure" grade) in the equivalent amount of perchloric acid and recrystallizing in the usual manner.

Our apparatus for determination of solubility is sketched in Fig. 1. The substance was stirred with solvent in beaker A in a Höppler ultrathermostat. After reaching equilibrium, a sample of solution was suction-filtered through a porous filter into cylinder B, from which it was forced with the help of bulb a through tube C into a small weighed glass. (Lower temperatures were reached by cooling the thermostat with iced water circulated through a coil.)

Solutions were analyzed for the cation by the standard methods: $Zn(ClO_4)_2$ by titration with potassium ferrocyanide [13], $Hg(ClO_4)_2$ by titration with potassium thiocyanate [14], $Cd(ClO_4)_2$ by the sulfate method [15], Ca, Sr and Mg by the sulfate method [16]; $Be(ClO_4)_2$ was analyzed for ClO_4^- ion by precipitation as $KClO_4$ in anhydrous alcohol with potassium acetate [17].

The time required for establishment of equilibrium was determined by successive withdrawal of samples at intervals of 1, 2, 4, 6, 8, 22 and 23 hours. In the case of perchlorates of Be, Mg, Ca, Sr, Cd and Hg, equilibrium was established after continuous stirring for 1-4 hours; in the case of Zn equilibrium was reached after 6-8 hours. Approach to equilibrium from above or below did not alter the result. Bearing in mind the great tendency of Sr perchlorate to form supersaturated solutions, the required temperature was approached only from below in the case of this salt.

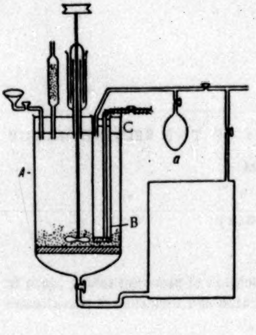

Figure 1. Apparatus for determination of solubility. (See text).

The composition of the solid phase was examined at the same time as the solubility was investigated. Solid phase was withdrawn from the solution with a glass sieve and pressed with filter paper between metal plates heated or cooled to approximately the temperature at which the solubility had been determined. A weighed amount of the expressed sample was analyzed for cation (for anion in the case of beryllium) and the result recalculated for $Me(ClO_4)_2 \cdot nH_2O$. In the majority of cases the excess of adsorbed water was 0-6 mole % of the total amount of water of crystallization (in the case of cadmium perchlorate the excess water was 10-13 mole % of the total water).

The perchlorates of Zn, Cd, Mg and Hg investigated are hexahydrates which do not change their composition in the 0 to 50° temperature range with the exception of zinc perchlorate which has the composition $Zn(ClO_4)_2 \cdot 7H_2O$ at temperatures below 20°. Sr perchlorate has the composition $Sr(ClO_4)_2 \cdot 3H_2O$ at a temperature above 25.7°. The change of composition of the solid phase is reflected on the solubility curves of Zn and Sr perchlorates (Figs. 2 and 3).

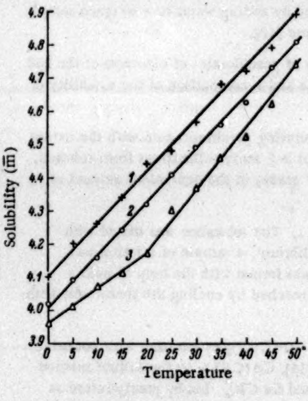

Figure 2. Solubility of $Mg(ClO_4)_2$ (1), $Cd(ClO_4)_2$ (2), $Zn(ClO_4)_2$ (3).

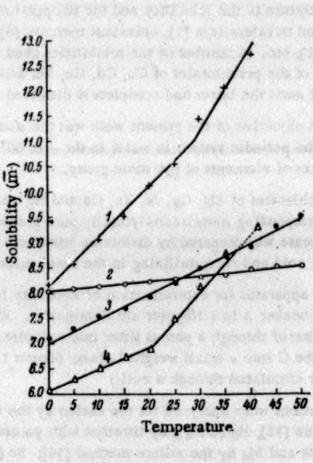

Figure 3. Solubility of $Sr(ClO_4)_2$ (1), $Be(ClO_4)_2$ (2), $Cd(ClO_4)_2$ (3), $Hg(ClO_4)_2$ (4).

The discontinuity on the solubility curve of mercuric perchlorate at 20° is not associated with a change of composition of the solid phase. Possibly it reflects a change of crystalline form (although no experimental evidence of this has been obtained).

TABLE 1

Solubilities of Perchlorates

Salt	Temperature											Literature data
	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	
$Be(ClO_4)_2$	8.02	8.08	8.10	8.16	8.20	8.26	8.29	8.35	8.45	8.48	8.52	7.07^{25° [11]
$Mg(ClO_4)_2$	4.10	4.20	4.26	4.34	4.44	4.48	4.57	4.68	4.72	4.79	4.89	4.50^{25° [2]
$Ca(ClO_4)_2$	7.10	7.29	7.51	7.67	7.91	8.18	8.46	8.76	8.88	9.29	9.50	7.89^{25° [1]
$Zn(ClO_4)_2$	3.97	4.01	4.07	4.11	4.17	4.3	4.37	4.46	4.52	4.62	4.74	—
$Sr(ClO_4)_2$	8.16	8.57	9.03	9.49	10.10	10.54	11.43	12.02	12.70	—	—	10.8^{25° [1]
$Cd(ClO_4)_2$	4.02	4.09	4.16	4.24	4.32	4.41	4.49	4.56	4.65	4.73	4.81	5.1^{14° [1]
$Hg(ClO_4)_2$	6.07	6.30	6.49	6.70	6.87	7.45	8.09	8.70	—	—	—	—
$Ba(ClO_4)_2$	4.11	—	—	—	5.29	—	—	—	6.13		—	5.9^{25° [4]

TABLE 2

Dependence of Logarithm of Mole Fraction of Aqueous Hydrate on the Reciprocal of the Absolute Temperature

Salt	$\frac{1}{T} \cdot 10^3$										
	3.660	3.594	3.531	3.470	3.411	3.353	3.298	3.244	3.192	3.142	3.094
$Be(ClO_4)_2 \cdot 4H_2O$	—0.5935	—0.5877	—0.5859	—0.5800	—0.5763	—0.5712	—0.5677	—0.5621	—0.5525	—0.5497	—0.5450
$Mg(ClO_4)_2 \cdot 6H_2O$	—0.9311	—0.9151	—0.9047	—0.8914	—0.8752	—0.8687	—0.8532	—0.8365	—0.8300	—0.8187	—0.8130
$Ca(ClO_4)_2 \cdot 4H_2O$	—0.6830	0.6769	—0.6426	—0.6271	—0.6030	—0.5782	—0.5516	—0.5233	—0.5120	—0.4735	—0.4618
$Zn(ClO_4)_2 \cdot 7H_2O$	—0.9024	—0.8945	—0.8831	—0.8752	—0.8639	—	—	—	—	—	—
$Zn(ClO_4)_2 \cdot 6H_2O$	—	—	—	—	—	—0.8982	—0.8867	—0.8722	—0.8623	—0.8462	—0.8268
$Sr(ClO_4)_2 \cdot 4H_2O$	—0.5800	—0.5412	—0.4980	—0.4547	—0.3973	—0.3554	—	—	—	—	—
$Sr(ClO_4)_2 \cdot 3H_2O$	—	—	—	—	—	—	—0.4558	—0.4180	—0.3748	—	—
$Cd(ClO_4)_2 \cdot 6H_2O$	—0.9440	—0.9333	—0.9225	—0.9080	—0.8948	—0.8801	—0.8671	—0.8548	—0.8413	—0.8283	—0.8156
$Hg(ClO_4)_2 \cdot 6H_2O$	—0.6175	—0.5812	—0.5507	—0.5165	—0.4887	—0.3895	—0.2699	—0.1401	—	—	—

Solubility data for the perchlorates investigated are presented in Table 1 and Figs. 2 and 3.

TABLE 3

Partial Molar Enthalpies and Entropies of the Phase Transition

Substance	ΔH (kcal/mole)	ΔS (cal/mole • degree)
$Be(ClO_4)_2 \cdot 4H_2O$ . . .	0.42	1.41
$Mg(ClO_4)_2 \cdot 6H_2O$ . . .	0.93	3.12
$Ca(ClO_4)_2 \cdot 4H_2O$ . . .	1.83	6.14
$Zn(ClO_4)_2 \cdot 6H_2O$ . . .	1.23	4.12
$Zn(ClO_4)_2 \cdot 7H_2O$ . . .	0.73	2.45
$Sr(ClO_4)_2 \cdot 4H_2O$ . . .	3.51	11.8
$Sr(ClO_4)_2 \cdot 3H_2O$ . . .	5.13	17.21
$Cd(ClO_4)_2 \cdot 6H_2O$ . . .	0.96	3.23
$Ba(ClO_4)_2 \cdot 3H_2O$ . . .	1.57	5.27
$Hg(ClO_4)_2 \cdot 6H_2O$ (I) . .	2.37	7.93
$Hg(ClO_4)_2 \cdot 6H_2O$ (II) .	8.03	26.91

The solubility, expressed as the number of moles of anhydrous substance per 1000 g solvent, increases linearly with the temperature. The logarithm of the mole fraction of aqueous hydrate changes linearly with the reciprocal of the absolute temperature (Table 2).

The partial molar enthalpies and entropies of the phase transition were calculated from the values of the tangents of the angles of slope of the logarithmic straight-line plots. Results are presented in Table 3.

No simple correlation in the change of values of solubility of the perchlorates of elements of the 2nd group is observed.

The enthalpies of the phase transition of perchlorates of elements of the subsidiary subgroup containing an equal amount of crystal water change in a similar manner to the changes of the sum of the 1st and 2nd ionization potentials. The regularities in change of enthalpy of the perchlorates of the main subgroup are more complex. This is probably due to another type of bond of the cation with the molecules of solvent both in solution and in the crystal form.

Crystal hydrates containing a larger number of molecules of water have a lower endothermic effect of the phase transition than the same perchlorates (zinc and strontium) with a smaller number of molecules of water. Evidently the establishment of a link between the phenomena investigated and the periodic law calls for additional data for both the nature of solutions and of the crystalline state.

SUMMARY

1. The solubility of perchlorates of elements of the 2nd group of the periodic system (except barium) was determined at 5° intervals in the 0 to 50° range.

2. A linear dependence of solubility (expressed in molalities) on temperature was established, likewise a linear relation between logarithm of concentration and 1/T, due to which the enthalpies and entropies of the phase transitions could be calculated.

3. An attempt was made to relate the observations with the periodic law.

LITERATURE CITED

[1] H. H. Willard and G. Smith, J. Am. Chem. Soc. 45, 286 (1923).

[2] E. Cornec and J. Dickeley, Compt. rend. 184, 1555 (1927).

[3] J. P. Simons and C. D. L. Ropp, J. Am. Chem. Soc. 50, 1650 (1928).

[4] Seidell, Solubility Inorg. Met. Org. Compounds (1940), I, 164.

[5] A. Rosenheim and S. Weinheber, Z. anorg. u. allgem. Chem. 69, 263 (1910).

[6] F. Calsolari, Gazz. 42, 11, 85 (1912).

[7] F. Lindstrand, Z. anorg. u. allgem. Chem. 230, 187 (1937).

[8] E. Newbery, Trans. Electrochem. Soc. 69, 611 (1936).

[9] A. E. Hill, J. Am. Chem. Soc. 43, 254 (1921).

[10] H. H. Willard and J. L. Kassner, J. Am. Chem. Soc. 52, 2391 (1930).

[11] N. V. Sidwick and N. B. Lewis, J. Chem. Soc. 129, 1287 (1926).

[12] Salvadori, Gazz. 42, I, 458 (1912).

[13] V. I. Petrashen, Volumetric Analysis (State Chemical Press, 1946), 180.

[14] I. M. Kolthoff and V. A. Stenger, Volumetric Analysis, (State Chemical Press, 1946), II, 421.

[15] W. Hillebrand and G. E. Lundell, Textbook of Inorganic Analysis (1935), 772.

[16] I. M. Kolthoff and E. V. Lundell, Quantitative Analysis (State Chemical Press, 1948), 772.

[17] Albert L. Chaney and A. Mann, J. Phys. Chem. 35, 2289 (1931).

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INTERACTION OF LITHIUM TITANATE WITH OTHER SALTS IN MELTS

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Lithium compounds are finding ever increasing application in the ceramic, glass and enamel industries. Use has also long been made in these industries of titanium dioxide and its derivatives (titanates of alkaline earth and other metals). The desire to clarify the mechanism of the processes involved in the production of ceramics, glasses and enamels has led investigators to study their physicochemical properties. Moreover the investigation of systems containing lithium titanate by the methods of physicochemical analysis is of fundamental interest in that it provides the opportunity for establishing an analogy between compounds of lithium and compounds of the alkali and alkaline earth metals, and also for determining the position of the TiO_3 ion in relation to other anions.

In this communication we present the results of an investigation of the interaction of lithium titanate with fluorides, chlorides, sulfates, silicates, pyrophosphates and some other salts of lithium, sodium and potassium in melts.

EXPERIMENTAL

Preparation and some properties of the starting salts. Li_2TiO_3 was prepared by sintering lithium carbonate with titanium dioxide. Analytically pure Li_2CO_3 was reacted with titanic acid which had previously been treated for 10 hours with 10% hydrochloric acid at the boil followed by thorough washing to eliminate the Cl ion and calcination at 1000°.

The titanium dioxide prepared in this fashion was almost spectrally pure, as shown earlier [1]. The stoichiometric mixture of Li_2CO_3 and TiO_2 was thoroughly stirred in a ball mill, pelleted, and calcined at 1200°. After a first calcination the pellets were reduced to powder and fresh pellets were pressed and subjected to a second calcination at 1200°. The resultant lithium titanate was ground to a fine powder and used in the investigation (m. p. > 1320°).

Na_2TiO_3 was obtained by fusing chemically pure Na_2CO_3 with TiO_2 at 1200° in a corundum crucible. The molten mass was held at 1200° for 20 hours. The melting point of the product was 1030°, in agreement with the literature data [2, 3].

K_2TiO_3 was prepared by fusing a stoichiometric mixture of titanium dioxide and previously recrystallized potassium carbonate (chem. pure) in a corundum crucible at 1000° for 20 hours. The resultant K_2TiO_3 was a white crystalline substance, very hygroscopic and rapidly deliquescing in the air. Potassium titanate which has been prepared in a platinum dish or crucible had a pink color due to formation of potassium platinotitanates. K_2TiO_3 prepared in a corundum crucible also acquires a pink color when melted in a platinum crucible. The melting point of K_2TiO_3 is 826° (the literature gives 806° [4] or 792° [5]).

$Li_4P_2O_7$ is prepared with great difficulty. Direct fusion of monoammonium phosphate with lithium carbonate does not lead to formation of the pyrophosphate; as a preliminary, therefore, to the preparation of lithium pyrophosphate by fusion of monoammonium phosphate with lithium carbonate, lithium metaphosphate was prepared, and this was then fused with lithium carbonate in the stoichiometric ratio at 1100°. M. p. of $Li_4P_2O_7$ 1000°.

The silicates of sodium, lithium and potassium were prepared by fusing pulverized quartz with the respective carbonates (chem. pure grades) after the latter had been recrystallized.

Melting points of the silicates: Na_2SiO_3 1090°; K_2SiO_3 969°; Li_2SiO_3 1201°.

$K_4P_2O_7$ was prepared by calcining dipotassium orthophosphate. M. p. 1090°.

The other salts used were the chem. pure or analytically pure grades, or were prepared by generally known methods.

Investigation was by the visual-polythermal method. Mixtures were melted in a platinum crucible in a resistance furnace. The temperature of start of crystallization was determined with the help of a platinum–platinum-rhodium thermocouple. All salts were previously dried and stored in a desiccator over sulfuric acid.

Results of Investigation and Their Evaluation

Lithium titanate is completely insoluble at temperatures up to 1100° in lithium salts with m. p. < 1100° (Li_2SO_4, Li_2MoO_4, Li_2WO_4, $LiPO_3$, LiCl and LiF). Even additions of 0.01% Li_2TiO_3 to these salts do not dissolve, and the melt crystallizes at the melting point of the pure salt. Mixtures of lithium titanate with Li_2SiO_3, Li_3PO_4 and Li_3VO_4 containing up to 15% Li_2TiO_3 do not melt at up to 1100°. The complete insolubility of lithium titanate in the majority of lithium salts indicates the similarity of its properties to those of barium titanate [6]. This similarity is manifested not only in the insolubility but also in a number of other properties. Thus, whereas the metatitanates of the alkali and alkaline earth metals form the following series in the order of falling melting points (given below the formulas)

$MgTiO_3$	$CaTiO_3$	$SrTiO_3$	$BaTiO_3$	Li_2TiO_3
?	1980 [7]	—	1610 [8]	> 1320
Na_2TiO_3	K_2TiO_3	Rb_2TiO_3	Cs_2TiO_3	
1030	826	760 [4]	698 [4]	

lithium titanate is situated between barium and sodium titanates; nevertheless the titanates are arranged in a series in accordance with the position of the metals in the periodic system from Mg to Ba and then from Li to Cs.

This order of alkali and alkaline earth metals is consistent with the arrangement of the liquidus curves of crystobalite in systems with alkali and alkaline earth metals [9], and also with the arrangement of the metals in the order of the effective charges of the cations in compounds [10].

Consequently, both in titanates and silicates, lithium is closer to barium than to beryllium and magnesium (contrary to what is observed with certain other salts).

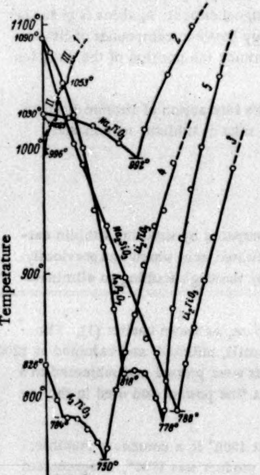

Figure 1. 1) $Li_4P_2O_7 - 2\,Li_2TiO_3$, 2) $Na_2TiO_3 - Li_2TiO_3$, 3) $Na_2SiO_3 - Li_2TiO_3$, 4) $K_2TiO_3 - Li_2TiO_3$, 5) $K_4P_2O_7 - 2\,Li_2TiO_3$.

The only lithium salt in which lithium titanate dissolves appreciably is the pyrophosphate. As we see from Fig. 1, the system $Li_4P_2O_7 - 2\,Li_2TiO_3$, which was studied up to 8.07% Li_2TiO_3, contains one eutectic and two transition points. The eutectic has the composition 0.5% Li_2TiO_3 and 99.5% $Li_4P_2O_7$ and melts at 996°. The transition points correspond respectively to 2.7% Li_2TiO_3 and 97.3% $Li_4P_2O_7$ and 5.2% Li_2TiO_3 and 94.8% $Li_4P_2O_7$; the respective melting points are 1025 and 1053°. The solubility of lithium titanate in pyrophosphate is associated with chemical interaction in the system. Phases I, II and III are probably binary compounds. Attention may be drawn to the slightly lower melting point of the eutectic mixture in comparison with the melting point of lithium pyrophosphate.

Lithium titanate has fairly high solubility in potassium and sodium titanates. For details see the table and Fig. 1.

1	2
$Li_4P_2O_7—2Li_2TiO_3$	
0	1000°
0.25	999
0.5	996
0.77	1010
1.03	1013
1.27	1016
1.57	1018
1.95	1020
2.13	1021
2.41	1023
2.70	1025
3.0	1035
3.3	1044
3.91	1049
4.54	1050
5.20	1053
6.58	1069
8.07	1073
$K_2TiO_3—Li_2TiO_3$	
0	826
2	798
4	784
6	783
8	774
10	764
12	759
14	805
16	836
18	866
20	907
22	938
24	950
26	989
$Na_2TiO_3—Li_2TiO_3$	
0	1030
5	1026
10	1020
15	1005
20	1015
25	1058
30	1097

1	2
$2KF—Li_2TiO_3$	
0	846°
1	834
3	818
5	807
7	798
10	784
13	769
16	757
17	740
20	725
22	704
24	691
25	679
27	658
30	742
35	856
40	950
$2NaF—Li_2TiO_3$	
0	994
1	980
3	968
5	954
10	928
15	905
18	886
20	874
22	864
24	848
25	861
27.5	897
30	927
32	950
$2RbF—Li_2TiO_3$	
0	790
2.5	787
5.0	777
7.5	758
10.0	745
12.5	731
15.0	709
17.5	695
20.0	679
22.5	669
25.0	658
27.5	723
30.0	805
35.0	909

1	2
$Na_2SiO_3—Li_2TiO_3$	
0	1090°
6	1005
8	988
12	938
16	897
18	866
20	847
22	836
24	812
26	788
28	827
30	856
32	893
34	928
36	960
$K_2TiO_3—2LiF$	
% K_2TiO_3	
100	826
95	759
90	716
85	751
80	886
75	928
70	960
65	993
$K_4P_2O_7—2Li_2TiO_3$	
0	1090
2	1078
4	1053
6	1027
8	1000
10	950
12	920
14	870
16	818
18	821
20	819
22	798
24	788
26	870
28	926
30	966
32	1000
36	1056

Note: In the table and diagrams: 1) equivalent % Li_2TiO_3; 2) temperature of start of crystallization.

The system $K_2TiO_3-Li_2TiO_3$ was studied up to 26% Li_2TiO_3. It contains one eutectic point at 11.5% Li_2TiO_3 and 750° and a transition point on the K_2TiO_3 branch at 784° and 3% Li_2TiO_3 – apparently, polymorphic transformation of K_2TiO_3, detected for the first time.

The system $Na_2TiO_3-Li_2TiO_3$ was studied up to 30% Li_2TiO_3. It contains one eutectic point at 18.5% Li_2TiO_3 and 992°. The phase of the composition above the eutectic is not lithium titanate; it is apparently a chemical compound of the components.

Experimental data for the systems Li_2TiO_3-2KF, Li_2TiO_3-2NaF, Li_2TiO_3-2RbF, $Li_2TiO_3-Na_2SiO_3$, $2Li_2TiO_3-K_4P_2O_7$ and K_2TiO_3-2LiF are presented in the table and in Figs. 1 and 2. These systems represent diagonal cuts of the corresponding ternary reciprocal systems.

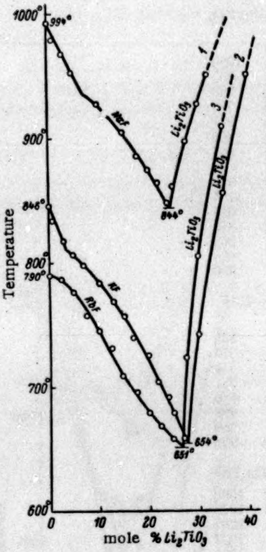

Figure 2. 1) $2NaF-Li_2TiO_3$, 2) $2KF-Li_2TiO_3$, 3) $2RbF-Li_2TiO_3$.

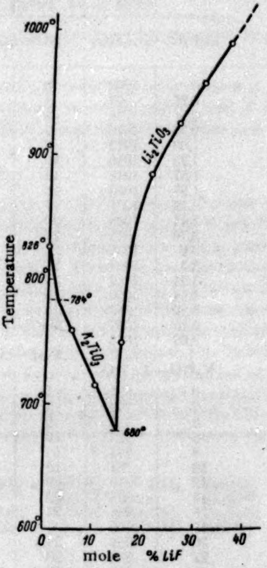

Figure 3. K_2TiO_3-2LiF.

The systems $2NaF-Li_2TiO_3$, $2KF-Li_2TiO_3$ and $2RbF-Li_2TiO_3$ are simple systems with a eutectic (Fig. 2). The eutectic mixtures contain respectively 24, 27.5, 26.5% Li_2TiO_3, and the melting points are 844, 654 and 651°. Transformations at 935 and 810° and 7.5 and 5% Li_2TiO_3 are observed on the NaF and KF crystallization branches respectively. The system $Li_2TiO_3-Na_2SiO_3$ also has a eutectic at 26% Li_2TiO_3 with m. p. 788°. The four systems mentioned thus form stable diagonal cuts of the corresponding reciprocal systems. The stability of the system $2KF-Li_2TiO_3$, for example, is confirmed by the fact that the system of the products of exchange $2LiF-K_2TiO_3$ (Fig. 3) does not have the form of the usual binary system with a eutectic – the right-hand branch corresponds to the crystallization of Li_2TiO_3.

The system $2LiF-K_2TiO_3$ could only be studied up to 27% LiF; on further increase of LiF content in the melts the product of exchange (Li_2TiO_3) is formed and is completely insoluble at 1100°. The part of the system adjacent to LiF is completely analogous to the system $2LiF-Li_2TiO_3$. In this region at higher temperatures, layering evidently occurs and extends into the reciprocal system from the $2LiF-Li_2TiO_3$ side.

The system $2Li_2TiO_3-K_4P_2O_7$ (Fig. 1) also proved to be an unstable section. The crystallization curve is complicated by the appearance of a new phase (the product of exchange) or by joining of the side of the square of compositions of the reciprocal system. This phase is limited by two transition points located at 16.0 and 23.5% Li_2TiO_3 and with melting points of 818 and 778°.

The stability of the pairs Li_2TiO_3-2KF, Li_2TiO_3-2NaF, Li_2TiO_3-2RbF and $Li_2TiO_3-Na_2SiO_3$ confirms the correctness of the position of the TiO_3 ion in the anionic series on the basis of polarizabilities in chemical compounds [10].

SUMMARY

1. It was shown by the fusion method that systems comprising lithium titanate and Li_2SO_4, Li_2MoO_4, Li_2WO_4, $LiPO_3$, LiCl and LiF do not exhibit reciprocal solubility up to 1100°, while systems with Li_2SiO_3, Li_3PO_4 and Li_3VO_4 do not melt at this temperature when the mixtures contain up to 15% Li_2TiO_3. An analogy between lithium titanate and barium titanate was established on the basis of the solubility of lithium titanate in the foregoing salts and on the basis of the melting points of the metatitanates.

2. It was established that the systems

$$Li_2TiO_3-2NaF,\ Li_2TiO_3-2KF,\ Li_2TiO_3-2RbF,\ Li_2TiO_3-Na_2SiO_3$$

are stable diagonal cuts of the corresponding ternary reciprocal systems.

LITERATURE CITED

[1] I. N. Belyaev, N. S. Novosiltsev, A. L. Khodakov and M. S. Shulman, J. Tech. Phys. 21, 547 (1951).

[2] E. W. Washburn and E. N. Bunting, Bur. Standards J. Research 12, 239 (1934).

[3] F. F. Barblan, Schweiz. mineralog. petrog. Mitt. 23, 295 (1943).

[4] Gm.-Kr. 41, 394 (1951).

[5] U. Nisioka, Sci. Repts. Tohoku Univ. 123, 259 (1934).

[6] M. P. Sholokhovich and I. N. Belyaev, J. Gen. Chem. 24, 218 (1954) (T. p. 219).*

[7] D. S. Belyankin, V. V. Lapin and N. A. Toropov, The Physicochemical Systems of Silicate Technology (Building Industry Press, 1954), 368.

[8] W. Trzebiatowski, M. Drys and J. Beran, Roczniki Chem. 28, 21 (1954).

[9] F. Kracek, J. Am. Chem. Soc. 52, 1346 (1930); Ann. Rept. Carnegie Inst. Year Book (1933), 63.

[10] I. N. Belyaev, Reports of the 3rd All-Union Conference on Physicochemical Analysis (USSR Academy of Sciences Press, 1955), 86.

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* T. p. = C. B. Translation pagination.

THE SOLUBILITY PRODUCT OF BERYLLIUM HYDROXIDE

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We found only one reference to the solubility product of beryllium hydroxide [1], according to which the solubility product of $Be_2O(OH)_2$ is $1 \cdot 10^{-40}$ at a solubility of $7.6 \cdot 10^{-8}$ mole/liter. This value is open to doubt, however, for the following reasons. The value cited relates not to the hydroxide but to a partly dehydrated substance:

$$2Be(OH)_2 \rightarrow H_2O + Be_2O(OH)_2.$$

Moreover, in calculating this product the assumption was made that the hydroxide was completely dissociated in its saturated solution. This assumption is scarcely admissible since beryllium hydroxide is a very weak base.

Calculation of the solubility product of beryllium hydroxide from the pH values of the solution at the start of its precipitation was also impossible because the concentrations of beryllium salt to which these data referred remained unknown. Again, different authors disagree about the pH of the start of precipitation of beryllium hydroxide [2, 3].

We employed the method of N. V. Akselrud and Ya. A. Fialkov [4] for determination of the solubility product of beryllium hydroxide. This consisted in dissolving the hydroxide in a solution of a salt of the corresponding metal, determining the cation concentration and measuring the pH in the solution. These data are sufficient for calculation of the solubility product: $SP = [Be^{++}]\,[OH^-]^2$. Substituting the concentration of hydroxyl ions by its value, we obtain: $SP = \frac{[Be^{++}]\,I^2}{[H^+]^2}$. Converting to the logarithm, we obtain (for room temperature): $\log SP = \log [Be^{++}] - 28 + 2pH$.

TABLE 1

Determination of Solubility Product of Beryllium Hydroxide (Gravimetric Method)

Experiment No.	Beryllium concentration (g-ion/liter) × $\times 10^2$	pH	Solubility product of $Be(OH)_2$ ($\times 10^{-18}$)	Experiment No.	Beryllium concentration (g-ion/liter) × $\times 10^2$	pH	Solubility product of $Be(OH)_2$ ($\times 10^{-18}$)
1	21.7	5.74	6.5	10	14.5	5.66	3.0
2	20	5.68	4.6	11	14	5.69	3.4
3	20	5.68	4.6	12	9.9	5.70	2.5
4	18.8	5.52	2.0	13	9.8	5.73	2.8
5	18.2	5.61	3.0	14	9.2	5.74	2.8
6	17.8	5.56	2.3	15	8.1	5.79	3.1
7	17.0	5.64	3.2	16	7.2	5.76	2.4
8	16.8	5.80	6.6	17	3	6.00	3.0
9	14.9	5.62	2.6	18	2.2	6.20	5.5

The beryllium hydroxide was prepared by treating beryllium nitrate solution with ammonia and washing the precipitate thoroughly with water. Solutions of beryllium nitrate of various concentrations (about 0.03-0.2M) were saturated at room temperature with the beryllium hydroxide. Saturation was effected by leaving the liquid in a closed vessel for 2-3 days with frequent shaking. The concentration of beryllium in the saturated solution was determined by the gravimetric method. The pH of the same solution was measured by the electrometric method. The solubility products of beryllium hydroxide calculated on the basis of these data are given in Table 1.

The mean value of the solubility product of beryllium hydroxide is $(3.5 \pm 1.4) \cdot 10^{-18}$.

In these experiments we could not observe an influence of the ionic strength of the solution on the solubility product of beryllium hydroxide. Fluctuations of the values of the solubility product with changing ionic strength of the solution probably come within the limits of experimental error.

The following series of determinations was performed by a similar method but with solutions of beryllium salt of much lower concentrations (about 0.001-0.002 M). In these solutions it is no longer possible to determine the beryllium concentration by the gravimetric method. Results are given in Table 2.

TABLE 2

Determination of Solubility Product of Beryllium Hydroxide
(Colorimetric Method)

Experiment No.	Concentration of beryllium (g-ion/l) × 10^3	pH	Solubility product of $Be(OH)_2$ (× 10^{-18})
1	1.99	6.45	1.6
2	1.8	6.48	1.6
3	1.5	6.50	1.5
4	1.3	6.52	1.4
5	1.0	6.68	2.3

In these experiments the mean value was $(1.7 \pm 0.3) \cdot 10^{-18}$ at room temperature. A slight influence of the ionic strength could now be observed; the ionic strength is here lower than in the experiments of Table 1 and the solubility product is correspondingly slightly lower. Consequently the activity product of beryllium hydroxide must be about $2 \cdot 10^{-18}$.

Since beryllium hydroxide is a weak electrolyte, its solubility cannot be calculated from the solubility product; we therefore determined the solubility of this compound by a direct method. The concentration of beryllium in a saturated aqueous solution of beryllium hydroxide was determined by a colorimetric method. Several determinations, agreeing satisfactorily with one another, led to a mean value of the solubility of $(2.2 \pm 0.1) \cdot 10^{-4}$ at room temperature.

Knowing the solubility product and the solubility of beryllium hydroxide, we could calculate the product of both of the dissociation constants of this compound: $Be(OH)_2 \rightleftharpoons Be^{\cdot\cdot} + 2OH'$, consequently $\frac{[Be^{\cdot\cdot}][OH']^2}{[Be(OH)_2]} = K_1 \cdot K_2$. The numerator in this expression is the solubility product of beryllium hydroxide, and the denominator is its solubility. Substituting the values obtained in the equation, we have:

$$K_1 \cdot K_2 = \frac{2 \cdot 10^{-18}}{2.2 \cdot 10^{-4}} = 9.1 \cdot 10^{-15}.$$

According to the literature [1], the second dissociation constant of beryllium hydroxide is $5 \cdot 10^{-11}$. From this we can calculate the value of the first constant:

$$K_1 = \frac{9.1 \cdot 10^{-15}}{5 \cdot 10^{-11}} = 1.8 \cdot 10^{-4}.$$

SUMMARY

1. Determination of the solubility product of beryllium hydroxide led to a value of $2 \cdot 10^{-18}$ at room temperature.

2. Determination of the solubility of beryllium hydroxide in water gave a value of $2.2 \cdot 10^{-4}$ mole/liter.

3. Calculation of the first dissociation constant of beryllium hydroxide gave a value of $1.8 \cdot 10^{-4}$.

LITERATURE CITED

[1] I. M. Kolthoff and V. A. Stenger, Volumetric Analysis (1950), 321.

[2] W. Hillebrand and G. E. Lundell, Applied Inorganic Analysis (1935), 90.

[3] H. T. S. Britton, Hydrogen Ions (1936), 292, 295, 314.

[4] N. V. Akselrud and Ya. A. Fialkov, Ukrain. Chem. J. 16, 294, 299 (1950).

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THE RECIPROCAL SYSTEM WITH LAYERING OF THE CHLORIDES AND TUNGSTATES OF LITHIUM AND SILVER

D. S. Lesnykh and A. G. Bergman

We have made a study of the ternary reciprocal system Li, Ag ‖ Cl, WO_4 in melts as a development of our theory that layering in the fused state is the consequence in the majority of cases of the differing structure of the outer electron layers in ions and the resultant marked difference of their polarization characteristics and of the physicochemical properties of the components of the stable pair [1]. Another objective of the investigation was the clarification of the influence on the character of reciprocal systems of replacement of divalent anions of SO_4'' in the layering system Li, Ag ‖ Cl, SO_4 [1] and of MoO_4'' in the layering system Li, Ag ‖ Cl, MoO_4 by the divalent WO_4'' anion. Diagonal cuts of the reciprocal system Li, Ag ‖ MoO_4, WO_4 were investigated to establish the effect on the reciprocal system Li, Ag ‖ Cl, WO_4 of replacement of the univalent Cl' ion by the divalent MoO_4'' ion. *

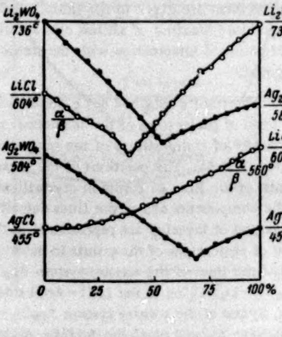

Figure 1. Fusion diagram of the binary systems AgCl – LiCl, $Ag_2Cl_2 - Ag_2WO_4$, $Li_2Cl_2 - Li_2WO_4$ and $Li_2WO_4 - Ag_2WO_4$.

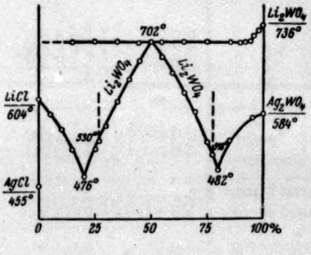

Figure 2. Diagonal cuts of the reciprocal system Li, Ag ‖ Cl, WO_4.

Binary systems. The fusion diagrams of the binary systems are plotted in Fig. 1. The system $Li_2Cl_2 - Li_2WO_4$ forms a eutectic at 37.5% Li_2WO_4 with m. p. 490°. The α, β-transformation of LiCl is observed at 560°.

The system AgCl – LiCl forms a continuous series of solid solutions [1, 2].

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* The experimental work was carried out jointly with E. P. Garmatina.

Cut number	Starting mixture of components	Melting point of starting mixture	Component added	Branches of curves of crystallization and their points of intersection							Layering			
				branch 1	PAC*	melting point	branch 2	intersection of 2 and 3		branch 3	start		end	
								PAC*	melting point		PAC*	melting point	PAC*	melting point
I	50% Ag_2Cl_2 + 50% Ag_2WO_4	455°	Li_2Cl_2	Ag_2WO_4	3.5	422°	Li_2WO_4	66	456°	[Li, Ag] Cl	5.5	519°	67.5	518°
II	62.5% Ag_2Cl_2 + 37.5% Ag_2WO_4	415	Li_2Cl_2	Ag_2WO_4	2	408	Li_2WO_4				2.5	530		
III	67.5% Ag_2Cl_2 + 32.5% Ag_2WO_4	400	Li_2Cl_2	Ag_2WO_4	1.5	375	Li_2WO_4				2	546		
IV	75% Ag_2Cl_2 + 25% Ag_2WO_4	406	Li_2Cl_2	Ag_2Cl_2	1	400	Li_2WO_4				1.5	580		
V	82.5 Ag_2Cl_2 + 17.5% Ag_2WO_4	424	Li_2Cl_2	Ag_2Cl_2	0.5	420	Li_2WO_4				1	610		
VI	75% Ag_2Cl_2 + 25% Li_2Cl_2	469	Ag_2WO_4	[Li, Ag] Cl	1	436	Li_2WO_4				2	570		
VII	50% Ag_2Cl_2 + 50% Li_2Cl_2	500	Ag_2WO_4	[Li, Ag] Cl	5.5	436	Li_2WO_4	67.5	476	Ag_2WO_4	8	505	67.5	500
VIII	10% Ag_2Cl_2 + 90% Li_2Cl_2	584	Li_2WO_4	[Li, Ag] Cl	32.0	485	Li_2WO_4							
IX	50% Li_2WO_4 + 50% Li_2Cl_2	553	Ag_2WO_4	Li_2WO_4	72.5	492	Ag_2WO_4				10	614	67.5	530
X	75% Li_2WO_4 + 25% Li_2Cl_2	668	Ag_2WO_4	Li_2WO_4							4	680		
XI	75% Li_2WO_4 + 25% Ag_2WO_4	644	Li_2Cl_2	Li_2WO_4							6	654		
XII	50% Li_2WO_4 + 50% Ag_2WO_4	536	Li_2Cl_2	Li_2WO_4	63.5	480	[Li, Ag] Cl				10	600	65	545

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* PAC = percent added component.

In the diagram of the systems $Li_2WO_4-Ag_2WO_4$ and $Ag_2WO_4-Ag_2Cl_2$ the eutectic points are located at 55.0 % Ag_2WO_4 and 560° and 70.0% Ag_2Cl_2 and 390° respectively. (Here and later all compositions are expressed in equivalent percentages.)

The diagonal cuts are plotted in Fig. 2. The components of the stable cut $Ag_2Cl_2-Li_2WO_4$ possess extremely limited reciprocal solubility in the fused state.

Layering is observed up to 94% Li_2WO_4 at 702°. In this interval the straight-line fusion plot is parallel to the axis of composition due to a three-phase monotectic process. The fusion diagram of the unstable $Li_2Cl_2-Ag_2WO_4$ cut comprises three crystallization branches: silver tungstate, lithium tungstate and solid solutions of [Li, Ag] Cl. Layering occurs in the region up to 26% at 530° and up to 86% Ag_2WO_4 at 510°. The fusion curve passes through a maximum at 702° with intersection with the stable diagonal.

Reciprocal system. The surface of the primarily separated crystals was investigated with the help of 12 internal cuts whose directions are shown in Fig. 3. Brief details of each of them are given in the table. The temperature maxima of all the cuts are at their points of intersection with the stable diagonal.

The results obtained are generalized in the form of projections of the isotherms on to the square of compositions of the reciprocal system (Fig. 4). The positions of the invariant points, of the lines of common crystallization of the components and of the lines demarcating the region of layering are represented in the form of projections of the points in question and of the lines of the ternary system $Ag_2Cl_2-Li_2Cl_2-Li_2WO_4$ on to the LiCl–AgCl side (Fig. 5) and of the ternary system $Ag_2Cl_2-Ag_2WO_4-Li_2WO_4$ on to the $Ag_2Cl_2-Ag_2WO_4$ side (Fig. 6). As we see from Fig. 4, the system consists of 4 fields of crystallization: the field of solid solutions of [Li, Ag] Cl, of silver chloride, of silver tungstate and of lithium tungstate.

The stable diagonal cut $Ag_2Cl_2-Li_2WO_4$ divides the square into two ternary systems: $Ag_2Cl_2-Ag_2WO_4-Li_2WO_4$ with a ternary eutectic, melting at 375°, and the system $Ag_2Cl_2-Li_2Cl_2-Li_2WO_4$ with solid solutions of [Li, Ag]Cl and lithium tungstate.

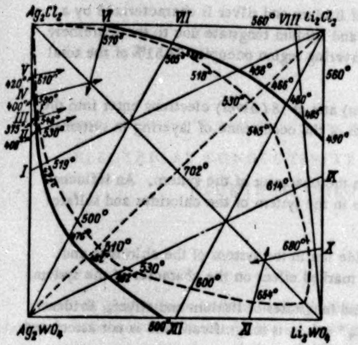
Ag₂Cl₂
VI
VII
560° VIII
Li₂Cl₂
560°
490°
IX
X
XI
XII
I
II
III
IV
V
420°
400°
375°
408
702°
614°
680°
654°
600°
500°
510°
530°
Ag₂WO₄
500°
Li₂WO₄

Figure 3. Distribution of internal cuts of the reciprocal system Li, Ag ‖ Cl, WO_4.

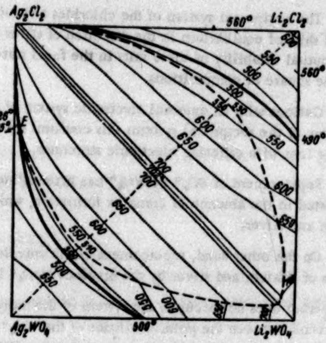
Ag₂Cl₂
560°
Li₂Cl₂
560°
490°
426°
375°
E
600
650
700
550
500
Ag₂WO₄
500°
Li₂WO₄

Figure 4. Projection of the fusion diagram of the reciprocal system Li, Ag ‖ Cl, WO_4 on to the square of composition.

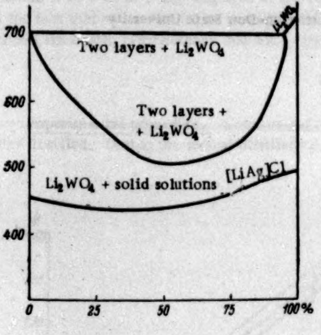

Figure 5. Projection of the field of crystallization and of the layering region on to the AgCl–LiCl side.

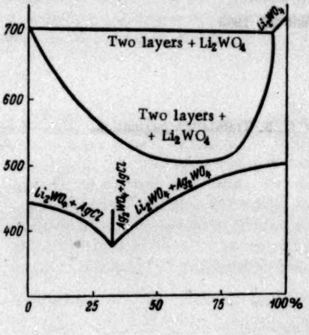

Figure 6. Projection of the field of crystallization and of the layering region on to the $Ag_2Cl_2 - Ag_2WO_4$ side.

Diagonal sections of the ternary reciprocal system of molybdates and tungstates of lithium and silver. The $Ag_2MoO_4 - Li_2WO_4$ diagonal has a transition point at 450° and 37.5% lithium tungstate; the $Li_2MoO_4 - Ag_2WO_4$ has a transition point at 460° and 67.5% silver tungstate. A polymorphic transformation was found in the case of lithium molybdate at 642°. Salts of both diagonals have unlimited reciprocal solubility in the fused state.

SUMMARY

1. The visual-polythermal method of physicochemical analysis was used in an investigation in melts of the ternary reciprocal system of the chlorides and tungstates of lithium and silver and of the diagonal sections of the ternary reciprocal system of the tungstates and molybdates of the same cations.

2. The reciprocal system of the chlorides and tungstates of lithium and silver is characterized by a one-sided shift of equilibrium in the direction of silver chloride and lithium tungstate due to the extremely limited mutual solubility of these salts in the fused state. The layering region occupies 63.51% of the total area of the square of compositions.

3. Cations with an external electronic system of 2 (lithium) and of 18 (silver) electrons enter into the composition of the reciprocal system; this confirms the hypothesis of the occurrence of layering in systems containing ions with differing electronic structures.

4. Replacement of SO_4'' by WO_4'' has little influence upon the character of the system. An influence is manifested in the absence of complex formation, which occurs in the system of the chlorides and sulfates of lithium and silver.

5. On the other hand, replacement of the univalent chloride ion in the system of the chlorides and tungstates of lithium and silver by the bivalent MoO_4'' ion has a marked effect on the character of the system.

Layering does not occur in the system of the molybdates and tungstates of lithium and silver. Evidently the difference between the polarizabilities of the WO_4'' and MoO_4'' anions is insignificant and is not associated with a large difference between the polarizabilities of the cations.

LITERATURE CITED

[1] D. S. Lesnykh and A. G. Bergman, J. Gen. Chem. 23, 373 (1953) (T. p. 383).*

[2] Technical Encyclopedia, Handbook of Phys. Chem. and Technological Constants (1931), 6.

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* T. p. = C. B. Translation pagination.

ELECTRICAL CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF ALUMINUM CHLORIDE IN NITROMETHANE*

V. S. Galinker

Solutions of aluminum halides in nitromethane have been studied to a much smaller extent than their solutions in nitrobenzene. It was earlier [1] observed that solutions of $AlCl_3$ and its complexes in nitromethane are very much more stable than solutions of $AlBr_3$ and its complexes in the same solvent.

Whereas solutions of $AlBr_3$ in nitromethane thicken fairly quickly when kept and are transformed into a gel [2] and their electrical conductivity progressively decreases, solutions of $AlCl_3$ do not alter in properties over a lengthy period. The electrical conductivity of $AlBr_3$ in nitromethane was studied by Ya. F. Mezhenny [3], but the electrical conductivity of $AlCl_3$ in nitromethane has not hitherto been studied. We have now investigated the electrical conductivity and viscosity of nitromethane solutions of $AlCl_3$ over a wide range of concentrations at several temperatures. $AlCl_3$ is readily soluble in nitromethane. According to our data, the solubility of aluminum chloride is 47% at 20°. Investigation of the electrical conductivity of this system is rendered particularly interesting by the fact that we have here an example of the formation of a conductive system from two non-conductive components, since both nitromethane and $AlCl_3$ (even in the fused state) are almost non-conductive.

EXPERIMENTAL

Experimental procedure. Commercial nitromethane was dried by standing over P_2O_5 for a week and was twice distilled. During the second distillation the nitromethane was charged directly into ampoules which were then sealed. The fraction distilling at constant temperature was used in the work. The $AlCl_3$ was the chem. pure grade. The density was determined with a pycnometer of 10 ml capacity. Viscosities were measured in the Ostwald viscometer. The viscosity was calculated from the formula $\eta = \eta_0 \frac{td}{t_0 d_0}$, where η_0, d_0, t_0 are the viscosity, density and period of discharge for water and η, d and t are the corresponding values for the solutions.

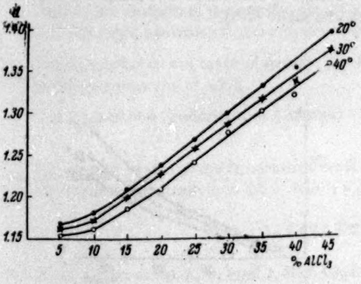

Figure 1. Density of $AlCl_3$ solutions in nitromethane.

The electrical conductivity was determined by the standard method in an apparatus with a tube generator. Temperature coefficients were calculated from the formulas

$$\alpha_{30-20} = \frac{x_{30°} - x_{20°}}{x_{30°} \cdot 10} \quad \text{and} \quad \alpha_{40-30} = \frac{x_{40°} - x_{30°}}{x_{30°} \cdot 10}$$

Viscosities and electrical conductivities were measured in a thermostat at 20, 30 and 40°. Temperatures were kept constant to within ± 0.1°. Measurements were performed in the concentration range of 5 to 45% $AlCl_3$.

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* L. Gorbachevskaya and I. Redchenko participated in the experimental work.

Solutions were made up in the following manner: A small quantity of aluminum chloride was transferred from an ampoule into the vessel for the solution, and the vessel was corked and weighed. Nitromethane was then run in from a small buret in quantity sufficient for a solution of the specified concentration. Considerable heat is released during the solution of $AlCl_3$.

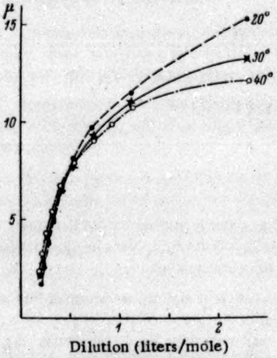

Figure 2. Molar electrical conductivity of solutions of $AlCl_3$ in nitromethane.

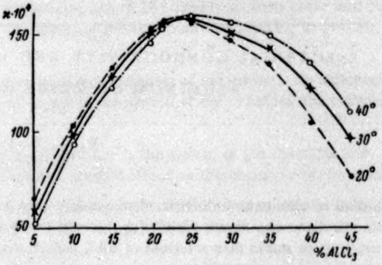

Figure 3. Specific electrical conductivity of $AlCl_3$ solutions.

The densities of solutions are plotted as a function of composition in Fig. 1. A straight-line plot is obtained over a wide interval of $AlCl_3$ concentrations. Figure 2 shows the change of molar electrical conductivity (μ) with increasing dilution of the solutions. It must be remembered, however, that these graphs have an arbitrary significance since the molar electrical conductivity was calculated on the basis of the normal molecular weight of aluminum chloride, whereas the possibility of association of $AlCl_3$ molecules in solution cannot be excluded. As we see from Fig. 3, the specific electrical conductivity for all three temperatures passes through a maximum at approximately 23% $AlCl_3$. The influence of temperature on the electrical conductivity of this system is extremely characteristic: up to the maximum point the temperature coefficient of electrical conductivity is negative, but after the maximum it changes its sign and becomes positive. Thus, the composition corresponding to the maximum must have a zero temperature coefficient. Change of sign of the temperature coefficient of electrical conductivity with change of concentration of solution is a rather rare phenomenon, and it reflects a complex interaction of solvent with solute [4-7].

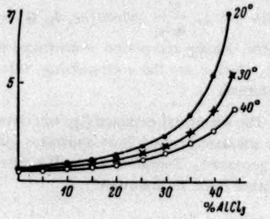

Figure 4. Viscosity of solutions of $AlCl_3$ in nitromethane.

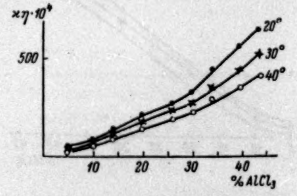

Figure 5. Change of product of electrical conductivity and viscosity with rising concentration of $AlCl_3$.

We have observed a change of sign of the temperature coefficient of electrical conductivity for solutions of CdI_2 in acetone and methylethyl ketone [8]. The change of sign can be explained on the basis of the theory of current-conducting complexes. The conductor in the system in question is the product of interaction of $AlCl_3$ molecules with solvent. The considerable thermal effect of solution of $AlCl_3$ in nitromethane testifies to energy changes during solvation. Processes of autocomplex formation and solvation proceed with evolution of heat, so that with rise of temperature the breakdown of the conducting complexes into non-conducting components must be intensified. Rise of temperature also leads, however, to fall in viscosity. Consequently, the negative temperature coefficient, observed up to 23%, may be the result of predominance in this region of the temperature effect leading to breakdown of the conductive complexes. The fall in viscosity with rising temperature in this region is insignificant. The influence of viscosity commences at above 23%, and the temperature coefficient of electrical conductivity becomes positive. Inspection of the viscosity plots (Fig. 4) confirms this explanation: the viscosity curves are smooth, rising slowly in the region of low concentrations and steeply in the region of more concentrated solutions. At low concentrations the isotherms are very close together and begin to diverge at higher concentrations. The curves show that the temperature coefficients of viscosity are small for weak solutions and increase with rising concentration.

The considerable rise in viscosity observed after 20-25% $AlCl_3$ is the cause of the reduced electrical conductivity in this region of concentration.

The supposition that the maximum on the electrical conductivity curve is due to the influence of viscosity is confirmed by Fig. 5 in which the product of specific electrical conductivity and viscosity is plotted as a function of the concentration of solution. The curves of Fig. 5 are not straight lines but are slightly convex to the axis of concentrations, although maxima are absent. This last fact is an indication that the viscosity is a dominating influence on the electrical conductivity but is not the sole factor. Some importance might be attached to the change of dielectric permeability of the solution with rising temperature, but this effect is evidently very minor.

SUMMARY

1. The electrical conductivity and viscosity of solutions of $AlCl_3$ in nitromethane were investigated at concentrations of 5 to 45% at 20, 30 and 40°.

2. Solutions of $AlCl_3$ in nitromethane possess appreciable electrical conductivity. The curves of specific electrical conductivity pass through a maximum at approximately 23% concentration of $AlCl_3$.

3. Plots of the products of the specific electrical conductivity and the viscosity are a series of nearly straight lines with slight convexity to the axis of composition.

4. The maximum on the curve of specific electrical conductivity is due to the sharp rise in viscosity with increasing concentration of $AlCl_3$.

5. The temperature coefficients of electrical conductivity are negative up to the maxima and positive thereafter.

6. The change of sign of the temperature coefficient of electrical conductivity may be explained on the assumption that the electrolyte in the system is a complex formed by addition of $AlCl_3$ to nitromethane.

LITERATURE CITED

[1] V. S. Galinker and A. V. Fiks, J. Gen. Chem. 25, 463 (1955) (T. p. 433). *

[2] Ya. F. Mezhenny, Memoirs Inst. Chem. Acad. Sci. Ukrain. SSR 3, 84 (1936).

[3] Ya. F. Mezhenny, Memoirs Inst. Chem. Acad. Sci. Ukrain. SSR 3, 361 (1936).

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* T. p. = C. B. Translation pagination.

[4] P. Walden, Electrochemie Nichtwässeriger Lösungen (1924), 151.

[5] V. A. Plotnikov and V. A. Izbekov, J. Russ. Phys. Chem. Soc. 43, 31 (1911).

[6] M. I. Usanovich, Trans. Sib. Phys.-Tech. Inst. 1 (3), 1 (1932); J. Russ. Phys. Chem. Soc. 59, 14 (1927).

[7] M. A. Klochko, Bull. Acad. Sci. USSR, Chem. Series 1938 , 971.

[8] V. S. Galinker, Bull. Kiev Polytech. Inst, 14, 156 (1953).

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INVESTIGATION OF THE REACTION OF PHENYLHYDRAZINE WITH CHLOROPHENOLS BY THE METHOD OF PHYSICO-CHEMICAL ANALYSIS

F. T. Pozharsky and D. E. Dionisyev

Investigation of the reaction of phenylhydrazine with cresols [1] showed that the position of the methyl group in the ring in relation to the phenolic hydroxyl group did not affect the reaction of the latter with phenylhydrazine. All three cresols form 1:1 compounds with phenylhydrazine. This is not inconsistent with previous conclusions about the composition of compounds of unsubstituted phenols with phenylhydrazine [2]. Furthermore, in a study of systems comprising phenylhydrazine and nitrophenols [3] it was established that the occurrence or absence of reaction of phenylhydrazine with the phenolic hydroxyl group depends on the relative position in the ring of the nitro group and the hydroxyl group. Absence of chemical interaction was found by physico-chemical analysis in the system phenylhydrazine-o-nitrophenol, whereas m- and p-nitrophenols form with phenylhydrazine the 1:1 compounds which are characteristic of monohydric phenols. These results prompted an investigation of the behavior toward phenylhydrazine of other ring-substituted phenols and in particular of those containing electronegative substituents.

In the present communication we describe the results of a study of the fusibility, density, viscosity and electrical conductivity of the systems phenylhydrazine-o-chlorophenol and phenylhydrazine-p-chlorophenol.

Materials and Experimental Procedure

The phenylhydrazine, twice-distilled in vacuum, had m. p. 20° and d_4^{30} 1.0920. o-Chlorophenol was purified by distillation at atmospheric pressure and had m. p. 7°, b. p. 175-176° and d_4^{45} 1.2300. p-Chlorophenol after distillation had m. p. 41°, b. p. 216° and d_4^{45} 1.2570.

Methods for determination of fusibility, density and viscosity have been described earlier [3]. Specific electrical conductivity was studied by the method of Kohlrausch. The source of alternating current was a two-stage tube generator of sonic frequency. A bridge was included in the circuit which permitted measurement of resistances up to 10^6 Ω. The mixtures for determination of electrical conductivity were placed in glass, hermetically closed cells with flat platinum electrodes. Separate mixtures were prepared for each determination. All determinations of properties in the liquid phase were performed in a thermostat at three temperatures at 10° intervals. The temperature was constant to within ± 0.1°.

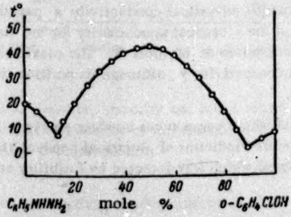

Figure 1. Fusibility of the system phenylhydrazine-o-chlorophenol.

System phenylhydrazine-o-chlorophenol. Results of measurement of the fusibility of this system are presented in Fig. 1. The fusion diagram contains two eutectic points corresponding to 8° and 87.5 mole % phenylhydrazine and 1° and 10 mole % phenylhydrazine, and also one maximum at 43° and 50 mole % phenylhydrazine, corresponding to the 1:1 compound of phenylhydrazine and o-chlorophenol. The flat maximum on the fusion curve indicates partial dissociation in the liquid phase of the congruently melting compound. Release of heat is observed on formation of the compound. Thus, the temperature rose from 20 to 40° when 20 g of mixture with 1:1 ratio of components was prepared. The compound forms colorless crystals which suffer no change when kept in the air for 10 days, whereas the pure components under these conditions turn brown and undergo appreciable changes in constants.

The first attempt to study the density and viscosity of the system phenylhydrazine-o-chlorophenol was made by Thole et al [4], but they only carried out determinations on five mixtures and these only at one temperature (50°). They found a maximum on the viscosity isotherm at 55 mole % phenylhydrazine. We made a detailed study of the viscosity and density of this system at 45, 55 and 65°.

Results of determinations of the density d and the viscosity η of the system and of the relative temperature coefficients of viscosity α are plotted in Fig. 2. The viscosity isotherms at 45, 55 and 65° pass through a maximum in the region of 40 mole % o-chlorophenol. These viscosity maxima are regularly displaced toward the side of the more viscous component (phenylhydrazine). The maxima on the curves of the temperature coefficient of viscosity, however, lie at 50 mole %. On the basis of these data we may infer that the 1:1 compound of phenylhydrazine and o-chlorophenol, which crystallizes nicely from the melt, is also stable in the liquid phase. The density isotherms are only slightly concave to the axis of composition and do not contain characteristic points.

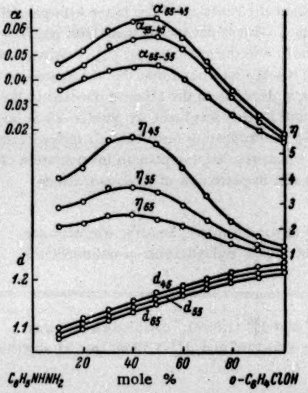

Figure 2. Density, viscosity and temperature coefficient of viscosity of the system o-chlorophenol-phenylhydrazine.

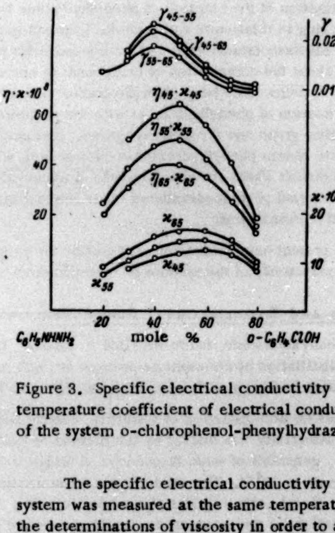

Figure 3. Specific electrical conductivity and temperature coefficient of electrical conductivity of the system o-chlorophenol-phenylhydrazine.

The specific electrical conductivity of the system was measured at the same temperatures as the determinations of viscosity in order to allow for the influence of viscosity on conductivity. Results are plotted in Fig. 3. According to M. A. Klochko's classification [5] both components can be classed as "non-conductors". The conductivity of their mixtures, however, increases as they approach the equimolecular ratio. The isotherms of specific electrical conductivity κ pass through a maximum in the region of 60 mole % o-chlorophenol. Correction of the electrical conductivity for the viscosity effect $\eta\kappa$ makes these curves more informative, with a pronounced maximum at 50 mole %. The maximum also persists on the curves of the temperature coefficient of electrical conductivity γ, although its position is slightly shifted in the direction of mixtures richer in phenylhydrazine.

The development of appreciable conductivity in a system both of whose components conduct poorly is evidence of chemical interaction, while the position of the maxima on the isotherms of electrical conductivity permits the conclusion that the current is conducted by the 1:1 compound which was detected by fusibility and viscosity measurements.

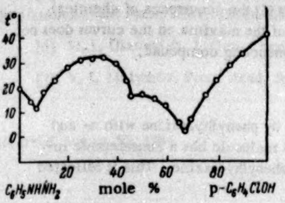

Figure 4. Fusibility of the system phenylhydrazine-p-chlorophenol.

System p-chlorophenol-phenylhydrazine. The fusibility diagram of this system (Fig. 4) contains three eutectics at 12, 16 and 2° and at 93, 55 and 33 mole % phenylhydrazine respectively. It also exhibits two maxima corresponding to 1 : 1 and 2 : 1 (two molecules of phenylhydrazine) compounds. The 1 : 1 compound crystallizes at 17° in the form of fine white crystals. The 2 : 1 compound forms colorless needles melting at 35° and gradually turning brown in the air. Both compounds are insoluble in water but readily soluble in ether.

The viscosity and density of the system was studied at 35, 45 and 55°. The viscosity isotherms (Fig. 5) and the curves of the temperature coefficient of viscosity pass through a conspicuous maximum at 50 mole %. This indicates that only the 1 : 1 compound is reflected on the viscosity isotherms. The viscosity of the compound falls rapidly with rising temperature from 13.30 centipoises at 35° to 4.64 centipoises at 55°. Since the difference between the viscosities of the pure components is insignificant, the displacement of the viscosity maxima with rising temperature is small and the curves are fairly symmetrical.

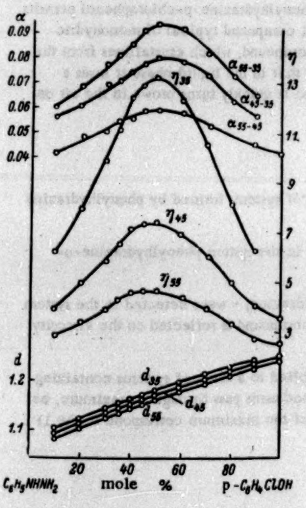

Figure 5. Density, viscosity and temperature coefficient of viscosity of the system phenylhydrazine-p-chlorophenol.

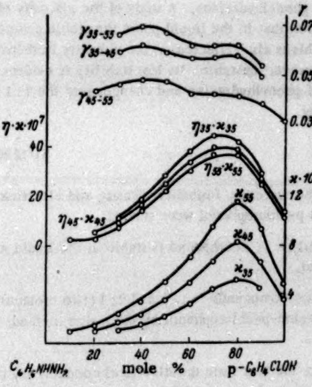

Figure 6. Specific electrical conductivity and temperature coefficient of electrical conductivity of the system phenylhydrazine-p-chlorophenol.

Results of measurements of the electrical conductivity of the system at the same temperatures are plotted in Fig. 6. The isotherms of specific electrical conductivity have a maximum in the region of 80 mole % p-chlorophenol. The maxima and their position are unchanged after correction of the electrical conductivity for viscosity. The curves of the temperature coefficient of the electrical conductivity are complex in form: they contain very flattened maxima and a minimum.

The appearance of a maximum on the electrical conductivity isotherms and its persistence when the electrical conductivity is corrected for the viscosity indicate according to [6] the occurrence of chemical interaction in the system. In the case in question, however, the position of the maxima on the curves does not provide an adequate basis for conclusions about the composition of the conducting compound.

Evaluation of Results

The experimental data obtained in the study of the systems formed by phenylhydrazine with o- and p-chlorophenols indicate that the introduction of chlorine into the phenol molecule has a considerable influence upon the nature of the interaction of the phenolic hydroxyl with phenylhydrazine. This is reflected in the composition and properties of the molecular compounds formed.

The presence of an intramolecular hydrogen bond has been demonstrated in o-chlorophenol by various methods [7]. It was expected that the presence of this bond would lead either to absence of reaction, as in the system with o-nitrophenol [3], or to weaker reaction. Experiments showed that the opposite occurred. Like unsubstituted phenol, o-chlorophenol forms a 1:1 compound with phenylhydrazine. This compound is more stable than the pure components: it is more stable at elevated temperature and can be stored for a long period in the air; it melts at a higher temperature than the components and is more clearly reflected on the fusion diagram.

Two compounds (1:1 and 2:1) were detected in the system phenylhydrazine-p-chlorophenol by the melting point method. A 2:1 compound (two molecules of phenylhydrazine) has here been detected for the first time in the monohydric phenol series. Phenol, cresols, nitrophenols and thymol form only a 1:1 compound with phenylhydrazine. A study of the viscosity of the system phenylhydrazine-p-chlorophenol permits the conclusion that in the liquid phase the stable compound is the 1:1 compound typical of monohydric phenols. This is also reflected on the viscosity isotherms. The 2:1 compound, which crystallizes from the melt, is, however, unstable. Its low stability is evidenced by the fact that in the liquid phase it loses a molecule of phenylhydrazine and changes into the 1:1 compound; also it quickly turns brown in the air on decomposing.

SUMMARY

1. The viscosity, fusibility, density and electrical conductivity of systems formed by phenylhydrazine with o- and p-chlorophenol were studied.

2. Only a 1:1 compound is stable in the liquid and solid phase in the system phenylhydrazine-o-chlorophenol.

3. Two compounds – 1:1 and 2:1 (two molecules of phenylhydrazine) – were detected in the system phenylhydrazine-p-chlorophenol by the fusion method; only the 1:1 compound is reflected on the viscosity isotherms.

4. For the first time the electrical conductivity method was applied to a study of systems containing phenylhydrazine. It was established that the electrical conductivity isotherms pass through a maximum, but only in the system phenylhydrazine-o-chlorophenol does the position of the maximum correspond to the 1:1 compound which was also detected by other methods.

LITERATURE CITED

[1] F. T. Pozharsky and D. E. Dionisyev, Sci. Memoirs Rostov State Univ., Trans. Chem. Faculty 20, 35 (1954).

[2] F. T. Pozharsky, Proceedings of the Scientific Conference to Mark the 80th Year of Existence of Rostov State University 1949, 63.

[3] D. E. Dionisyev and F. T. Pozharsky, J. Gen. Chem. Supp. Vol. 1, 219 (1953).

[4] Thole, Mussell and Dunstan, Trans. Chem. Soc. 103, 1108 (1913).

[5] M. A. Klochko, Trans. 2nd All-Union Conference Electrochemistry (Academy of Sciences of the Ukrainian SSR Press, Kiev, 1949), 320.

[6] M. I. Usanovich, J. Gen. Chem. 10, 959 (1940).

[7] V. I. Malyshev, Proc. Acad. Sci. USSR 24, 675 (1939).

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THE INFLUENCE OF SPECIFIC ADSORPTION ON THE HALF-WAVE POTENTIAL DURING REDUCTION OF COMPLEX COMPOUNDS

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The principles of application of the polarographic method to the determination of the structure and instability constants of complex compounds were first stated by Heyrovsky and Ilkovic [1]. The authors started from the assumptions that: 1) the process of reduction at the dropping mercury electrode is reversible; 2) simple ions formed by dissociation of the complex are discharged at the cathode.

Under these conditions the following equations are valid:

$$\varphi_{1/_2 k} - \varphi_{1/_2} = \frac{RT}{zF}\ln K_c - p\frac{RT}{zF}\ln C_x^0, \tag{1}$$

$$\varphi_{1/_2 k} - \varphi_{1/_2} = \varphi^0_{1/_2 k} - \varphi^0_{1/_2} - p\frac{RT}{zF}\ln C_x^0, \tag{2}$$

$$\frac{\Delta\varphi_{1/_2 k}}{\Delta \log C_x^0} = -p\frac{RT}{zF}, \tag{3}$$

where $\varphi_{1/2\,k}$ is the half-wave potential of the reduction of the metal of the complex compound; $\varphi_{1/2}$ is the same for the metal of solutions of simple salts; $\varphi^0_{1/2\,k}$ is the standard potential of the electrode reaction with participation of the complex ion; $\varphi^0_{1/2}$ ditto for the electrode reaction with participation of the simple ion; K_c is the instability constant of the complex; C_x^0 is the concentration of the free addend in solution; $\underline{p}$ is the coordination number; $\underline{z}$ is the number of electrons taking part in the reduction reaction; R is the gas constant; T is absolute temperature; F is the Faraday number. The work of Heyrovsky and Ilkovic [1] has been followed by a large number of publications on the application of the polarographic method to the determination of the coordination number and of the instability constant of complex compounds.

It follows from Equations (1) and (2) that the relation between the logarithm of the concentration of free addend and half-wave potential must be a linear one. This is confirmed experimentally only when the above assumptions hold good. These assumptions, however, are not always valid.

In Fig. 1 the half-wave potential of reduction of a metal ion is plotted as a function of the logarithm of the concentration of the free addend on the basis of data of I. A. Korshunov et al [2]. It is seen that the dependence is not linear; the half-wave potential increases more rapidly than the logarithm of the concentration of free addend. However, the authors regarded the starting assumptions as indisputable, and they divided the curves into a number of sections approximating to straight lines, and calculated the coordination numbers and instability constants of a series of hypothetical complexes; here the main criterion of splitting of the curve into rectilinear portions was the requirement that the coordination number obtained by the calculation should be a whole integer.

I. A. Korshunov and N. I. Malyugina [3] found four complexes with coordination numbers of 2, 3, 4 and 6 in a solution of copper nitrate and pyridine. Why was it then impossible to detect other copper-pyridine complexes, and in particular a copper-pyridine complex with a coordination number of 5 when dividing the curve into a series of arbitrary and approximately rectilinear portions ?

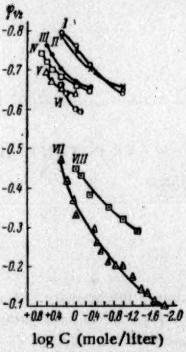

Figure 1. Dependence of the half-wave potential of a metal ion on the logarithm of the concentration of the addend (from data of I. A. Korshunov et al).
1) Cd−HI, 2) Cd−KI, 3) Cd−HBr,
4) Cd−NH_4CNS, 5) Cd−NaCl,
6) Pd−KI, 7) Cu-pyridine,
8) Hg−KI.

It must be noted that not one of the authors (either those mentioned in this paper or those not mentioned) who have studied the complexes polarographically has isolated from the solution the hypothetical complex compound whose coordination number and instability constant were determined; nor has its composition been established by chemical methods.

A different opinion is expressed by A. N. Frumkin and G. M. Florianovich [4] who consider that in many cases the complex ion is discharged at the electrode and that previous dissociation of the complex into simple ions is not essential for the discharge.

The hypothesis of the complete reversibility of processes at the mercury electrode is true for a limited number of ions and can hardly be extended to complex ions if they do not directly take part in the electrode reaction.

Experiment shows that discharge of the majority of simple ions is accompanied by appreciable polarization (inhibition of the discharge process). This will apply to an even greater extent to complex ions. Discharge and ionization proceed with finite velocity, i.e., only those molecules or ions enter into reactions which possess a certain excess of energy. Consequently, the direct participation of a complex molecule or ion in an electrode reaction is associated with the need for activation of these particles, and the process must therefore be irreversible.

The general picture of the cathode process is further complicated by the occurrence of specific adsorption. Many simple ions and even more complex ones are susceptible to specific adsorption.

The following can be adsorbed on the dropping mercury electrode: 1) addends; 2) discharging complex ions or molecules; 3) particles which are both addends and complexes.

Equations for the half-wave potentials in the case of specific adsorption of an addend or other particles were given by V. L. Kheifets [5] on the basis of A. N. Frumkin's theory of retarded discharge.

In this case the half-wave potential during reduction is determined by the following equation:

$$\varphi_{1/2} = -\frac{RT}{\alpha zF}\ln D + \frac{RT}{\alpha zF}\ln k - \frac{(z_k - \alpha z)}{\alpha z}\psi_1, \qquad (4)$$

where $\varphi_{1/2}$ is the half-wave potential; D is the constant of diffusion to the surface of the electrode under the experimental conditions; $\underline{k}$ is the velocity constant of discharge; z_k is the valence of the complex cation; $\underline{z}$ is the number of electrons participating in the electrode reaction; α is a fractional coefficient; ψ_1 is the mean value of the potential in solution at a distance of one ionic radius from the surface of the metal.

For the case of participation of anions in the cathode process the half-wave potential equation acquires the form:

$$\varphi_{1/2} = -\frac{RT}{\alpha zF}\ln D + \frac{RT}{\alpha zF}\ln k + \frac{z_k - \alpha z}{\alpha z}\psi_1. \qquad (5)$$

But if molecules participate in the discharge, then the correction factor for the concentration in the double layer can be omitted and the half-wave potential equation may be written:

$$\varphi_{1/2} = -\frac{RT}{\alpha zF}\ln D + \frac{RT}{\alpha zF}\ln k + \psi_1. \tag{6}$$

In the absence of specific adsorption, the ψ_1 potential is substantially equal to zero and the equation for the half-wave potential becomes:

$$\varphi_{1/2} = -\frac{RT}{\alpha zF}\ln D + \frac{RT}{\alpha zF}\ln k. \tag{7}$$

Thus, in the presence of adsorbed particles the half-wave potential changes in proportion to the change in the ψ_1 potential, and the latter in turn depends upon the concentration of the substances being adsorbed [Equations (4), (5) and (6)].

In the case of a reversible electrode process in the absence of substances susceptible to specific adsorption, the half-wave potential is independent of the concentration of dissolved substance, and is governed only by the properties of the discharging particle [Equation (7)].

Figure 1, Curve VII, shows the half-wave potential during discharge of the pyridine complex of copper as a function of the pyridine concentration according to data of Korshunov and Malyugina [3].

Pyridine is known to be adsorbed like a cation-active substance, i.e., the ψ_1 potential has a positive sign. Copper enters into the complex cation in the pyridine complex.

Consequently, as we see from Equation (4), the half-wave potential in this case must be displaced toward the negative side, as shown on the curve.

Curves I-VI and VIII in Fig. 1 show the dependence of the half-wave potential for discharge of complex anions on the concentration of the addend according to data of I. A. Korshunov et al [2]. In these cases the anion was surface-active, i.e., the sign of ψ_1 was negative.

Consequently, as we see from Equation (5), the half-wave potential should again be shifted toward the negative side, as is actually the case.

The regularities considered above change to a marked extent if the discharging particle is itself susceptible to adsorption on the surface of the electrode. When the substance tends to be specifically adsorbed, its concentration on the surface of the electrode may be determined from the equality of the electrochemical potentials of a substance at the surface of an electrode and in the mass of the solution at equilibrium. In the present case the standard chemical potentials of a substance at the surface of an electrode and in the mass of a solution will not be identical.

During discharge of an adsorbed cation, the concentration of substance at the surface of an electrode is related to the concentration of substance in the mass of the solution by the following expression [5]

$$C_s = C_0 e^{\frac{\Phi - zF\psi_1}{RT}}, \tag{8}$$

where C_s is the concentration of substance at the electrode surface, C_0 is the concentration of substance in the mass of solution, Φ is the molar free energy of adsorption of particles by the surface of the metal.

The rate of discharge of ions according to the theory of retarded discharge may be expressed by the equation:

$$i = kC_0 e^{\frac{\Phi - zF\psi_1}{RT}} \cdot e^{\frac{-\alpha zF(\varphi - \psi_1)}{RT}} \tag{9}$$

If $\alpha + \beta = 1$, we obtain

$$\varphi = \frac{RT}{\alpha zF} \ln k + \frac{RT}{\alpha zF} \ln C_0 + \frac{\Phi}{\alpha zF} - \frac{\beta}{\alpha} \psi_1 - \frac{RT}{\alpha zF} \ln i. \tag{10}$$

Thus the half-wave potential corresponding to the value $i = \frac{i_{pr}}{2} = \frac{DC_0}{2}$ may be expressed by the equation

$$\varphi_{1/2} = \frac{RT}{\alpha zF} \ln \frac{2k}{D} + \frac{\Phi}{\alpha zF} - \frac{\beta \psi_1}{\alpha}. \tag{11}$$

Under otherwise identical conditions, the higher the adsorption potential Φ, the more positive will be the potential of discharge.

In the case of adsorption and discharge of an anion, we have

$$C_s = C_0 e^{\frac{\Phi + zF\psi_1}{RT}}. \tag{12}$$

The corresponding half-wave potential will be:

$$\varphi_{1/2} = \frac{RT}{\alpha zF} \ln \frac{2k}{D} + \frac{\Phi}{\alpha zF} + \frac{1 + \alpha}{\alpha} \psi_1. \tag{13}$$

When a molecule is adsorbed and discharged, the concentration of adsorbed particles is given by

$$C_s = C_0 e^{\frac{\Phi}{kT}}. \tag{14}$$

The rate of discharge of a molecule is:

$$i = kC_0 e^{\frac{\Phi}{RT}} \cdot e^{-\frac{\alpha zF}{RT}(\varphi - \psi_1)}, \tag{15}$$

and hence the half-wave potential is:

$$\varphi_{1/2} = \frac{RT}{\alpha zF} \ln \frac{2k}{D} + \frac{\Phi}{\alpha zF} + \psi_1. \tag{16}$$

Since the absolute value of the adsorption potential Φ is always greater than the ψ_1 potential (which also leads to increase of concentration in the double layer), a rise of adsorption potential Φ will cause, in accordance with Equations (11), (13) and (16), a displacement of the half-wave potential toward the positive side, i.e., the better the discharging ions or molecules are discharged, the more positive will be their discharge potential. In cases when the magnitude of the adsorption potential remains constant, which happens when particles of one sort are discharged, their concentration will exert an influence upon the displacement of the half-wave potential due to change of the ψ_1 potential.

It has thus been shown that the half-wave potential must depend upon the susceptibility of a complex ion or molecule to specific adsorption. The susceptibility to specific adsorption is usually higher for particles with a high dipole moment. The possibility therefore arises of polarographic differentiation between cis- and trans-isomers. Attempts to differentiate between cis- and trans- forms of complex compounds on the basis of the half-wave potential were made by Holtzclaw [6] and Holtzclaw and Sheetz [7] who thought that the different half-wave potentials of cis- and trans- forms may be due to the large orientation of the cis-form in the field around the mercury drop, which might facilitate discharge. These authors did not consider the influence of change of structure of the double layer during adsorption on the rate of discharge and the half-wave potential.

In his first paper Holtzclaw carried out measurements with the cis- and trans- isomers of dinitrotetramminecobalt (III) chloride in presence of potassium chloride, potassium tartrate and potassium citrate; he detected both a difference in the half-wave potentials of the two isomers and an influence of the concentration of the additives on the half-wave potential. In the solutions studied by Holtzclaw the complex cations as well as the anions of the additives could be adsorbed, and this greatly complicates the analysis of his results. In the second paper [7] a study was made of different cis- and trans-isomeric cobalt complexes under the same conditions as in the first paper; however, the authors did not go further in their conclusions.

For our investigation we took cis- and trans-isomers of dinitrotetramminecobalt (III) chloride, dinitrobisethylenediaminecobalt (III) nitrate, di- and monohydrates of cobalt glycolate and acicular and lammellar forms of copper glycolate.

The cis- and trans- isomers of the first two compounds were selected because the geometrical isomerism of these salts was established with difficulty and is a classic example of this type of isomerism. Polarographic investigation of these compounds may lead to a new method of determination of the structure of geometrical isomers. We synthesized all the compounds used in this investigation. The table gives analyses and references to methods of preparation of the substances used.

Substance	Percent of metal ion bound in complex form		Method of preparation
	theoretical	experimental	
$[Co(NH_3)_4(NO_2)_2]Cl$			
trans	23.17	23.26	Jorgensen [8]
cis	23.17	23.22	
$[CoEn_2(NO_2)_2]NO_3$ *			
trans	17.70	17.66	Werner [9]
cis	17.70	17.52	
$CoGl_3H_2O$ **	19.71	19.76	Ley and Winkler [10]
$CoGl_3 2H_2O$	18.60	18.48	
Acicular form	27.69	27.62	Mauthner and Suida [11]
Flat form	27.69	27.64	

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* En = ethylenediamine

** $Gl = NH_2CH_2COO^-$.

Polarograms were plotted with a visual polarograph. The cathode was a dropping mercury electrode and the anode a mercurous sulfate electrode. The substance under test was dissolved in 0.1 N potassium sulfate solution which served as a background. Gelatin was used to develop the maxima.

Polarograms were plotted at various concentrations of substances.

Examination of the half-wave potentials of reduction of the various complex compounds showed that: a) the process of their reduction is irreversible; b) due to the specific adsorption of the reduced particles at the surface of the mercury, a dependence of the half-wave potential on the concentration of reduced substance is observed.

Figures 2 and 3 clearly illustrate the dependence of the half-wave potential on the concentration of cis- and trans-isomers of dinitrotetramminecobalt (III) chloride and dinitrobisethylenediaminecobalt nitrate. The higher polarity of the cis-isomers leads to their greater adsorption and consequently to a higher positive value of the potential of the first half-wave, corresponding to the reduction of trivalent cobalt to divalent. The possibility of identification of cis- and trans-isomers by the polarographic method has thus been proved.

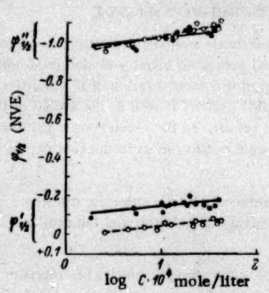

Figure 2. Half-wave potential as a function of the concentration of $[Co(NH_3)_4(NO_2)_2]Cl$. (dense lines are the trans-form; broken lines are cis).

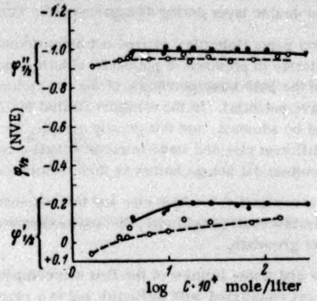

Figure 3. Half-wave potential as a function of the concentration of $[CoEn_2(NO_2)_2]NO_3$ (dense lines trans-form, broken lines cis)

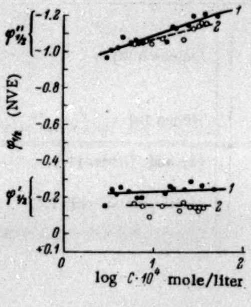

Figure 4. Half-wave potential as a function of the concentration of cobalt glycolate.
1) $CoGl_3 \cdot H_2O$, 2) $CoGl_3 \cdot 2H_2O$.

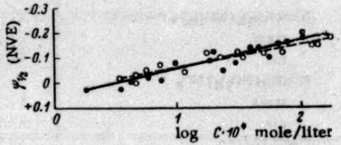

Figure 5. Half-wave potentials as a function of the concentration of copper glycolate (the dense line is the acicular form, the broken line is the lamellar form).

Figure 4 reveals a definite difference between the potentials of the first half-waves in the case of the two modifications of cobalt glycolate. The higher positive value of the potential of the first half-wave of the dihydrate indicates that this complex is the cis-isomer, in agreement with the results of A. A. Grinberg and V. P. Ogoleva [12] which were obtained by chemical methods.

Figures 2, 3 and 4 show that reduction of trivalent cobalt to divalent leads to breakdown of the complex, and the potentials of the second half-wave then become very similar.

The half-wave potential is plotted as a function of the concentration of copper glycolate in Fig. 5. The half-wave potentials of both modifications are seen to lie on the same curve, indicating the similarity between dipole moments of the acicular and lamellar forms, and in turn the absence of cis- and trans-isomerism in aqueous solution.

The authors express their deep gratitude to V. L. Kheifets for advice and assistance in the work.

SUMMARY

1. Discharge of a complex at the dropping mercury electrode is by no means always realized with a reversible equilibrium potential.

2. In the case of a retarded discharge stage of a complex: a) the specific adsorption of the addend displaces the half-wave potential in a direction governed by the sign of the charge of the ion and the sign of the adsorption potential; b) the specific adsorpiton of the discharging ion itself leads to a sharp displacement of the half-wave potential in the positive direction.

3. Cis- and trans-isomers differ in their susceptibility to specific adsorption. Advantage can be taken of this difference to identify these isomers from the magnitude of the half-wave potential.

LITERATURE CITED

[1] J. Heyrovsky and D. Iklovic, Collection Czechoslov. Chem. Communs. 7, 198 (1935).

[2] I. A. Korshunov et al., J. Gen. Chem. 16, 1573 (1946); 19, 2045 (1949) (T. p; 513 a)*; 20, 402, 1962 (1950) (T. p. 425, 2031)*; 21, 615, 620 (1951) (T. p. 685).*

[3] I. A. Korshunov and N. I. Malyugina, J. Gen. Chem. 20, 402 (1950) (T. p. 425).*

[4] A. N. Frumkin and G. M. Florianovich, Proc. Acad. Sci. USSR 80, 907 (1951).

[5] V. L. Kheifets, D. K. Avdeev and L. S. Reishakhrit, Textbook of Theoretical Electrochemistry (Leningrad State University Press, 1954).

[6] H. F. Holtzclaw, J. Am. Chem. Soc. 73, 1821 (1951).

[7] H. F. Holtzclaw and D. P. Sheetz, J. Am. Chem. Soc. 75, 3053 (1953).

[8] S. M. Jorgensen, Z. anorg. Chem. 5, 162 (1894); 17, 469, 473 (1898).

[9] A. Werner, Ann. 386, 1, 248 (1911).

[10] H. Ley and H. Winkler, Ber. 42, 3894 (1909).

[11] Mauthner and Suida, Monatsh. 11, 375 (1890).

[12] V. P. Ogoleva, Dissertation (Leningrad Lensovet Institute of Technology, 1953).

Received July 9, 1955.

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THE COMPOSITION OF COMPLEX COMPOUNDS OF COBALT WITH DIMETHYLGLYOXIME FORMED IN PRESENCE OF Na_2SnO_2

L. S. Nadezhina and P. N. Kovalenko

The reaction of complex formation between an ion of divalent cobalt and dimethylglyoxime (H_2Dm) was discovered by L. A. Chugaev at the start of the 20th century. This reaction is still the center of interest both to chemists working in the field of complex compounds and to analysts who exploit the reaction in colorimetry. This interest persists because in spite of the considerable experimental material accumulated in recent years the composition of the complex compounds of divalent cobalt with H_2Dm cannot be said to be fully clarified. There is even some controversy as to the valence of the cobalt playing the part of complex former during the reaction.

Feigl [1], Hieber and Leutert [2] and Thilo and Heilborn [3] believed that the cobalt is divalent and bound non-ionogenically to a molecule of H_2Dm entering into the composition of the complex. Chugaev [4] and Sen and Ray [5], on the other hand, believed that in the absence of a reducing agent the cobalt is oxidized to the trivalent state and then enters into reaction with dimethylglyoxime. This hypothesis was confirmed by Babko and Korotun [6] who showed that in the absence of a reducing agent the cobalt forms with H_2Dm a compound $H[Co(HDm)_2Cl_2]$ which possesses acidic properties and changes in an alkaline medium into $[Co(HDm)_2ClH_2O]$. As the authors point out, in the absence of air the reaction of formation of $H[Co(HDm)_2Cl_2]$ does not go either with or without heating for several days; this provides direct proof that cobalt enters into the complex compound in the oxidized state.

The mechanism of reaction of cobalt with H_2Dm changes appreciably when substances with reducing properties are introduced into the solution. The presence in the solution of Na_2SO_3, $NH_2OH \cdot HCl$, hydrazine, etc. intensifies the color of the complex compound of cobalt with dimethylglyoxime, and the shade changes from yellow-green to yellowish brown. Babko and Korotun [6] succeeded in synthesizing the dimethylglyoximine of Co^{2+} in presence of hydroxylamine as reducing agent. Analysis of their compound showed that it may be represented by the formula $Co(HDm)_2 \cdot 8\,H_2O$.

The reaction of cobalt with H_2Dm proceeds quite differently in presence of such reducing agents as Na_2S and Na_2SnO_2. Even traces of cobalt in the solution then lead to formation of a deep-violet complex compound [7] which is unstable and easily changes into the brown compound of Babko and Korotun on heating, shaking or standing in the air. In an acid medium the solution becomes perfectly colorless, but the color is restored when NaOH is added. A bluish-violet compound with the formula $CoS \cdot H_2Dm \cdot NH_3 \cdot H_2O$ could be isolated from a solution containing Co^{2+}, Na_2S, NH_4OH and H_2Dm [1]. Further investigations, however, did not confirm these results.

V. N. Podchainova and V. I. Butorin [8] made a close study of the reaction of cobalt with H_2Dm in presence of Na_2SnO_2 and NH_4OH and confirmed the high sensitivity of this reaction for the cobalt ion and the poor stability.

It is clear from the foregoing survey that the reaction of cobalt with dimethylglyoxime is extremely complex and is influenced not merely by the acidity of the medium but also by the nature of the reducing agent.

In the present work we made an experimental study of the reaction of divalent cobalt with dimethylglyoxime in presence of sodium stannite in an alkaline and an ammoniacal medium. The results permit an evaluation of the composition of the complex and of the limits of applicability of this reaction in colorimetric analysis.

EXPERIMENTAL

The work was carried out with the FEK-2 photoelectrocolorimeter equipped with a galvanometer with a sensitivity of $5 \cdot 10^{-7}$ A. The optical density of the solution (D) was determined by a differential method 5 minutes after preparation of the solution, using a light filter whose characteristics were 610, 550, 500 and 450 mμ. Parallel studies were made in alkaline and ammoniacal media; the concentration of cobalt in the final volume was kept equal to $0.8 \cdot 10^{-4}$ M (alkaline medium) and $1.6 \cdot 10^{-4}$ M (ammoniacal medium), while the concentrations of reactants were: H_2Dm 0.02 M, NH_4OH 0.8 M, NaOH 0.5 M, Na_2SnO_2 0.5 M.

Investigation of the character of the light extinction of the solution in various parts of the spectrum. In order to be able to compare the absorptivity of the complex compound formed on reaction of cobalt with H_2Dm in presence of Na_2SnO_2 with the usual yellowish-brown complex of Co^{2+} with H_2Dm, and also for the purpose of determining its molar coefficient of absorption (ϵ), we studied the curves of light absorption that characterize the relative sensitivity of the reaction in various parts of the spectrum (Fig. 1). The results of these investigations showed that the color intensity of the complex compound formed by the Co^{2+} ion with H_2Dm in presence of Na_2SnO_2 falls appreciably when NH_4OH is introduced into the solution, and at the same time the stability of the color also alters. In an alkaline medium the color of maximum intensity is developed within 5-10 minutes and remains unchanged for a long period; in an ammoniacal medium on the other hand, the optical density of the solution begins to decrease after only 10-12 minutes, and decolorization sets in after 1-2 hours (see table).

Duration (min.)	1.0	3.0	5.0	10.0	20.0	30.0	60.0	120.0
D (alkaline medium)	0.310	0.345	0.380	0.380	0.378	0.380	0.380	0.370
D (ammoniacal medium)	0.280	0.310	0.320	0.320	0.300	0.280	0.216	0.135

Decolorization of the solution in an ammoniacal medium can be accelerated by heating or vigorous shaking, as shown by Podchainova and Butorin [8]. In an alkaline medium such measures have no effect on the optical

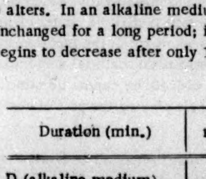

Figure 1. Absorption spectra of the dimethylglyoxime complex in an alkaline (1) and ammoniacal (2) medium. Na_2SnO_2 concentration 0.5 M.

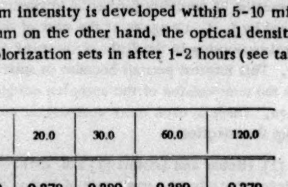

Figure 2. Dependence of the optical density on the cobalt concentration of the solution.
1) Alkaline medium; 2) ammoniacal medium (concentration of H_2Dm 0.02 M, of Na_2SnO_2 0.5 M)

density of the solution, as evidenced by the considerably greater stability of the complex under these conditions. A linear dependence of the optical density of the solution on the cobalt concentration is observed both in an alkaline and ammoniacal medium in the cobalt concentration range of $0.2 \cdot 10^{-5}$ to $2 \cdot 10^{-5}$ M (Fig. 2). With increasing dilution of the solution ($CoSO_4$ concentration of $< 0.2 \cdot 10^{-5}$ M) the value of ϵ falls slightly, due to increasing degree of dissociation of the complex; this is especially characteristic in an ammoniacal medium. Nevertheless the maximum deviation from the mean value does not exceed ± 10 % (rel.). The maximum of the light absorption remains in the same position with increasing dilution, indicating the stability of the complex compounds in question, in spite of the apparent change of color from violet to pink with progressive reduction of the cobalt concentration of the solution.

Physico-chemical analysis of the composition of the dimethylglyoxime complex of Co^{2+} in an alkaline and ammoniacal medium. With the objective of clarifying the mechanism of reaction of cobalt with dimethylglyoxime in presence of Na_2SnO_2 in an alkaline and ammoniacal medium, we made use of the method of physico-chemical analysis of the colored solutions (according to Ostromyslensky and Job).

The following systems were studied: $CoSO_4 - H_2Dm$ (in an alkaline and an ammoniacal medium with constant Na_2SnO_2 concentration), $CoSO_4 - NH_4OH$ (with constant concentration of Na_2SnO_2 and H_2Dm).

Solutions of various equimolar concentrations ($0.8 \cdot 10^{-3}$, $1.0 \cdot 10^{-3}$, $1.2 \cdot 10^{-3}$ M) were studied in various parts of the spectrum (λ 450, 500, 550, 610 mμ). In all cases similar results were obtained with more or less characteristic maxima on the composition/property curves.

Curves obtained when working with a green light filter (λ 500 mμ) and an initial concentration of components of the system of $1 \cdot 10^{-3}$ M (other conditions as before) are plotted in Fig. 3.

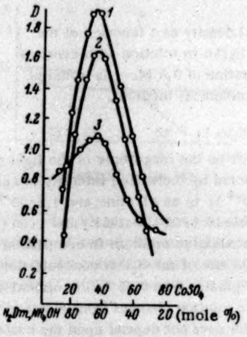

Figure 3. Optical density as a function of composition of the system.
1) $CoSO_4 - H_2Dm$ (Na_2SnO_2 0.5 M, NaOH 0.5 M), 2) $CoSO_4 - H_2Dm$ (Na_2SnO_2 0.5 M, NH_4OH 0.8 M), 3) $CoSO_4 - NH_4OH$ (Na_2SnO_2 0.5 M, H_2Dm 0.03 M); λ 550 mμ, l 1.7 cm.

The results of physico-chemical analysis lead to the conclusion that in presence of Na_2SnO_2 and in an alkaline and ammoniacal medium, cobalt reacts with two molecules of H_2Dm on the same lines as in the formation of the normal yellowish-brown complex of Co^{2+} (Fig. 3, Curves 1 and 2) [9].

Two molecules of NH_3 enter into the composition of the inner sphere of the complex, in addition to dimethylglyoxime, in an ammoniacal medium, as reflected on the maximum of the curve characterizing the optical density of the system $CoSO_4 - NH_4OH$ with constant concentration of Na_2SnO_2 and H_2Dm (Fig. 3, Curve 3). Neutral molecules of water probably penetrate the inner sphere of the complex, in place of ammonia, in an alkaline medium, due to which the spectrophotometric characteristics of the complex are altered and the color stability increases. The probability of replacement of NH_3 by OH' is extremely small since NaOH does not influence the optical density of the solution in the region of concentrations commensurate with cobalt.

Our investigations using constant concentration of dimethylglyoxime and with variation of the $CoSO_4/Na_2SnO_2$ ratio within narrow limits showed that in all cases of commensurability of concentrations of the components of the system, the violet color was not developed and the usual yellowish-brown complex of cobalt with dimethylglyoxime was formed. These results support the statement of Coronato [7] that stannite does not directly participate in the complex formation but serves only to maintain the cobalt in the divalent state.

Investigation of the influence of H_2Dm, Na_2SnO_2, NaOH and NH_4OH on the color intensity of cobalt-dimethylglyoxime. The nature of the influence of Na_2SnO_2 on the magnitude of the optical density of the solution may be determined by carrying out experiments at constant concentration of cobalt and of all other components of the system (H_2Dm, NH_4OH and NaOH) with exception of Na_2SnO_2, and gradually increasing the concentration of the latter. It is then found that the violet color does not appear when the concentration of Na_2SnO_2 is less than $2.5 \cdot 10^{-3}$ M, and that the normal yellowish-brown compound of Co^{2+} with H_2Dm is formed. The color of the solution changes in the range of $3 \cdot 10^{-3}$ to $0.5 \cdot 10^{-2}$ M Na_2SnO_2, the violet color predominating. The reaction is sharply displaced in the direction of formation of the violet complex when the Na_2SnO_2 concentration is greater than $0.2 \cdot 10^{-2}$ M, and the intensity of light absorption increases up to 0.4 M Na_2SnO_2 and then remains constant. Under these conditions the reaction can be utilized for quantitative colorimetric determination of cobalt (Fig. 4).

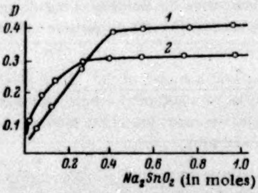

Figure 4. Influence of Na_2SnO_2 on the intensity of light absorption of dimethylglyoxime complexes of cobalt in an alkaline (1) and an ammoniacal (2) medium.

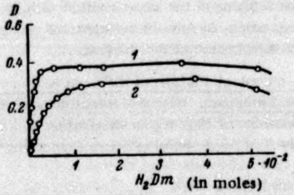

Figure 5. Optical density as a function of the concentration of H_2Dm in solution with constant Na_2SnO_2 concentration of 0.5 M. 1) Alkaline medium, 2) ammoniacal medium.

Investigation of the influence of the concentration of dimethylglyoxime on the magnitude of the light extinction of the solution established that increasing concentration is accompanied by increasing intensity of color which reaches its limit at a concentration of H_2Dm in the solution of $3.6 \cdot 10^{-3}$ M in an alkaline, and $1.2 \cdot 10^{-2}$ M in an ammoniacal medium, corresponding respectively to a $CoSO_4/H_2Dm$ ratio of 1:30 (in alkali) and 1:50 (in ammonia). These results indicate the greater stability of the complex in the alkaline medium in comparison with that in the ammoniacal medium, as was pointed out above. With further rise of the H_2Dm concentration the color intensity does not change and, finally, at a concentration of H_2Dm greater than 0.05 M the optical density of the solution gradually starts to fall. At the same time the color of the solution changes from violet to reddish-brown (Fig. 5). The H_2Dm concentration range within which the color does not depend upon the content of dimethylglyoxime in solution is $0.35 \cdot 10^{-2}$ to $4.0 \cdot 10^{-2}$ M in an alkaline medium and $1.2 \cdot 10^{-2}$ to $4.0 \cdot 10^{-2}$ M in an ammoniacal medium. Cobalt can be quantitatively determined if these conditions are maintained.

On the basis of the method of limited logarithmic plotting, the above data enabled us to calculate the number of molecules of dimethylglyoxime entering into reaction with cobalt. It was thus established that the tangent of the angle of slope of the straight line obtained by plotting log D against log C_{H_2Dm} (numerically equal to the number of molecules of H_2Dm entering into the composition of the complex) is nearly two. This is fully consistent with the results of physico-chemical analysis (Fig. 6).

Examination of the curves of dependence of optical density of the solution on the concentration of NH_4OH and NaOH (Fig. 7) shows that whereas even a small quantity of NH_4OH sharply reduces the intensity of color of the solution, the effect of NaOH is only manifested when the concentration is more than 1 M. The explanation is that the structure of the complex changes when NH_4OH is introduced into the solution, whereas NaOH evidently has no influence on the mechanism of the process. It should be specially noted that the color stability is a direct function of the NH_4OH concentration of the solution and that decolorization sets in the more rapidly the higher is the NH_4OH concentration.

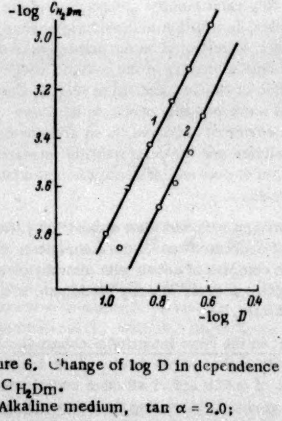

Figure 6. Change of log D in dependence on log C_{H_2Dm}.
1) Alkaline medium, $\tan \alpha = 2.0$;
2) ammoniacal medium, $\tan \alpha = 2.1$.

In connection with the application of the reaction in colorimetric analysis, the data permit the conclusion that NH_4OH is undesirable in the solution because the sensitivity of the reaction is halved, the degree of dissociation of the complex increases, and the color ceases to be stable. In cases, however, when the introduction of NH_4OH into the solution is unavoidable during the analysis, satisfactory results can be obtained if the above data are taken into consideration. A harmful effect of NaOH upon the results of colorimetric determination of cobalt is excluded because in practice the NaOH concentration of the solution usually does not exceed 1 M.

Evaluation of Results

On the basis of the experimental data presented above, the composition of the complex formed by reaction of Co^{2+}, NH_4OH and H_2Dm in presence of Na_2SnO_2 in the solution may be represented by the formula $[Co(HDm)_2 \cdot 2\,NH_3]$.

If, in place of HDm^-, this compound were to contain Dm^{2-} anions formed as a result of subsequent dissociation of HDm^-, which is a reasonable assumption when caustic alkali is present in the solution, then we should naturally expect the color intensity of the solution to increase with rising concentration of NaOH in the solution. This is not found in practice. Conversely, in the region of high concentrations of NaOH, where precisely the conditions most favorable to formation of a neutral salt of dimethylglyoxime are created, an appreciable fall in color intensity is observed (Fig. 7). For final confirmation that the above-mentioned complex does not carry a charge, additional experiments were carried out which established that the boundaries of the colored layer are not shifted when the investigated colored solution is electrolyzed in a U-tube (the supporting electrolyte used was a solution containing H_2Dm, Na_2SnO_2 and NH_4OH in the same concentrations as in the solution under examination).

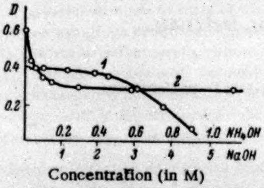

Figure 7. Dependence of light extinction of a solution of cobalt-dimethylglyoxime complex on the concentration of NaOH (1) and NH_4OH (2) in presence of 0.5 M Na_2SnO_2.

There are grounds for assuming that in an alkaline medium in the absence of NH_4OH a complex of analogous composition is formed in which the role of addend is played by two molecules of H_2O in place of neutral NH_3 molecules. We find some support for this hypothesis in the paper of Babko and Korotun [6]. These authors, investigating the composition of the complex compound of Co^{2+} with H_2Dm formed in presence of hydroxylamine and corresponding to the formula $Co(HDm)_2 \cdot 8\,H_2O$, observed that the crystals rapidly darken when gradually dried at 105° and decrease in weight due to loss of water. Under these conditions it is highly probable that $[Co(HDm)_2 \cdot 2\,H_2O]$ is formed to some extent; the latter has a deep violet color, and this is responsible for the darkening of the originally yellow crystals.

Isolation in the pure form of $[Co(HDm)_2 \cdot 2\,NH_3]$, as well as of the analogous complex of Co^{2+} with H_2Dm, formed in presence of Na_2SnO_2 in a solution not containing NH_4OH, is impossible due to their poor stability in the air.

SUMMARY

1. A study was made of the composition of the complex compound of Co^{2+} with H_2Dm in presence of Na_2SnO_2 in an ammoniacal and an alkaline medium, using the physico-chemical method of analysis.

2. Data obtained by physico-chemical analysis were confirmed by calculation of the number of coordinated HDm^- groups by the method of limited logarithmic plotting.

3. Molar coefficients of extinction of dimethylglyoxime complexes of Co^{2+}, formed in presence of Na_2SnO_2, were calculated. It was established that in an ammoniacal medium the sensitivity of the reaction is half of that in an alkaline medium.

4. Optimum conditions were established for the formation of the dimethylglyoxime complex of Co^{2+} in presence of Na_2SnO_2. These conditions may be recommended for the quantitative colorimetric determination of cobalt.

LITERATURE CITED

[1] F. Feigl and L. Tustanowska, Ber. 57, 762 (1924).

[2] W. Hieber and F. Leutert, Ber. 60, 2296 (1927).

[3] E. Thilo and H. Heilborn, Ber. 64, 1441 (1951).

[4] L. A. Chugaev, Selected Works (Acad. Sci. USSR Press, 1954), I.

[5] D. C. Sen and P. Ray, Chem. Zentr. 1936, I, 4885.

[6] A. K. Babko and M. V. Korotun, J. Gen. Chem. 24, 597 (1954) (T. p. 609). *

[7] L. Rossi and R. G. Coronato, C. A. 37, 5673 (1943).

[8] V. N. Podchainova and V. I. Butorin, Trans. Comm. Anal. Chem. III (VI), 261 (1951).

[9] L. S. Nadezhina and P. N. Kovalenko, Proc. Acad. Sci. USSR 101, 1073 (1955).

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* T. p. = C. B. Translation pagination.

THE THERMAL STABILITY OF PARAFFINIC HYDROCARBONS

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A powerful stimulus to study of the thermal stability of hydrocarbons and of the mechanism of their decomposition was given by the development of hydrocarbon cracking processes. Many investigators have collected data for the quantitative transformations of hydrocarbons in dependence on the temperature and duration of cracking [1]. The kinetic aspect of the problem has been considered in later papers [2]. On the basis of thermodynamic calculations it has been shown [3] that at 25° hydrocarbons of normal structure are less stable than their iso-analogs. With rising temperature the stability of iso hydrocarbons falls, and at 700° and higher the normal hydrocarbons become more stable than the corresponding iso compounds.

Existing literature data for the limits of thermal stability of paraffinic hydrocarbons are extremely contradictory. Thus, differences of up to 100° in the initial temperatures of breakdown have been reported. The literature is lacking in any data for the initial temperatures of thermal dissociation of the paraffinic hydrocarbons of gasolines, and also in data obtained under uniform conditions, i.e. comparable data for the behavior in the internal combustion engine. The present investigation was undertaken with the objective of filling this gap in our knowledge and in particular of determining the temperature threshold of decomposition of paraffinic hydrocarbons.

Hydrocarbon	Boiling point	n_D^{20}	d_4^{20}	Temperature of initial decomposition
n-Pentane	36.3°	1.3578	0.6270	270—275°
n-Hexane	68.5	1.3750	0.6609	230—235
n-Heptane	98.0	1.3874	0.6830	210—215
n-Octane	124.5	1.3970	0.7022	195—200
n-Nonane	149.5	1.4050	0.7166	185—190
2,2,4-Trimethylpentane	99.5	1.3918	0.6916	295—300
3-Methylheptane	119	1.3985	0.7052	210—215
2-Methyloctane	143.5	1.4033	0.6974	200—205

The hydrocarbons whose constants are set forth in the table above were selected for determination of the initial temperatures of decomposition. A quartz tube, length 63 cm and diameter 3.5 cm, heated in an electric furnace, was used for decomposition of the hydrocarbons. Before feeding into the quartz tube, the substance was charged into a vaporizer where the temperature was held at 15-20° above the boiling point of the hydrocarbon. The same feed rate of approximately 0.14 g/min was maintained for all the hydrocarbons. Feeding of the hydrocarbon was effected by displacement with mercury from a small buret. Products of transformation were collected in a receiver immersed in a freezing mixture, and were later passed, via an efficient cooling coil, into a gasholder. The experimental temperatures were measured simultaneously with a copper-constantan thermocouple and a quartz thermometer. The entire system was purged and filled with nitrogen before each experiment, and the quartz tube was heated in a strong air stream after the experiment.

Of all the generally known methods of determination of olefins, the most acceptable in respect of consistency of results under our conditions was the quantitative bromide-bromate method. At certain appropriate values of the bromine numbers (since they could be governed both by addition reactions and by substitution reactions), the condensate was analyzed in parallel for the hydrogen numbers, which only characterize the addition reactions.

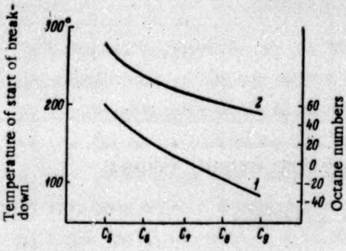

Fig. 1. Normal hydrocarbons.
1) Octane numbers; 2) breakdown temperatures.

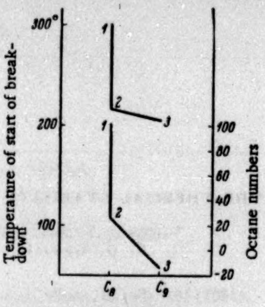

Fig. 2. Iso hydrocarbons.
1) 2,2,4-Trimethylpentane; 2) 2-methylheptane; 3) 2-methyloctane

We took account of the temperature of decomposition of the hydrocarbons which corresponded to hydrogen numbers of 0.4-0.6 for the condensed product. Determination of the initial temperatures of decomposition of the 8 hydrocarbons in question required over 90 experiments and analyses of the products, since the originally broad temperature intervals of the lower and upper values were gradually narrowed to 5°. The experimental results are given in the table. The relation between the temperature of initial thermal breakdown of the hydrocarbons and their octane numbers is plotted in Figs. 1 and 2.

SUMMARY

1. Initial temperatures of thermal breakdown under identical conditions were determined for n-pentane, n-hexane, n-heptane, n-octane, n-nonane, 2-methylheptane, 2,2,4-trimethylpentane and 2-methyloctane.

2. The initial temperatures of breakdown of normal hydrocarbons are lower than the corresponding temperatures of the iso-analogs under the chosen conditions.

3. A fall in the initial temperature of breakdown with rising molecular weight is found for normal paraffinic hydrocarbons.

4. The degree of branching of the hydrocarbons favorably influences their thermal stability. Isooctane (2,2,4-trimethylpentane) is distinguished by exceptional thermal stability.

5. A direct relation is found between the octane numbers of the investigated hydrocarbons and their thermal stability.

LITERATURE CITED

[1] Calingaert, J. Am. Chem. Soc. 45, 130 (1923); Haber, Ber. 29, 2691 (1896); Haber and Samoylowicz, Chem. Zentr. 1896, 777.

[2] A. I. Dintses, Progr. Chem. 1934, 936; A. I. Dintses and A. V. Frost, J. Gen. Chem. 3, 747 (1933).

[3] Rossini, Crude Oils (Oxford University Press), Vol. V, p. 1.

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CONJUGATED SYSTEMS

LXII. THE CONDENSATION OF DIENIC HYDROCARBONS WITH PROPIOLIC ACID AND ITS METHYL ESTER

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Among the numerous dienic syntheses described in the literature, relatively little attention was paid, until recently, to reactions with participation of acetylenic compounds. In the series of preceding papers in this field, communications were made on the interaction of dienic hydrocarbons with the simplest acetylenic carbonyl compounds – propargylaldehyde and butynone [1,2]. The first member of the series of acetylenic acids (propiolic acid) and its esters have scarcely been studied as dienophiles. Only the reactions of this acid with cyclopentadiene [3] and of its methyl ester with dihydronaphthalene [4] have been described.

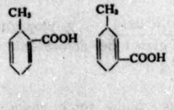
We resolved to make a more detailed investigation of the condensation of propiolic acid and its methyl ester with dienic hydrocarbons – butadiene, piperylene, isoprene, cyclohexadiene-1,3, and also with 2-chlorobutadiene-1,3. Condensation was found to proceed faster with the acid than with its methyl ester.

Butadiene and propiolic acid gave $\Delta^{1,4}$-dihydrobenzoic acid (I); butadiene and methyl propiolate gave the methyl ester of acid (I). Saponification of the latter gave acid (I), identical in properties with that obtained by the first reaction. Acid (I) had been isolated by Alder and Backendorf [5] as a secondary product in the condensation of butadiene with acetylene dicarboxylic acid.

As expected from the proposed structure, acid (I) does not react with maleic anhydride, adds on bromine with formation of a crystalline dibromide, and changes into benzoic acid when heated with sulfur.

It was earlier shown that the primary products of condensation of acetylenic aldehydes and ketones with dienic hydrocarbons are capable of isomerizing into compounds with conjugated double bonds. Such an isomerization would be particularly expected in the condensation of dienic hydrocarbons with acetylenic acids, since acids are usually susceptible to migration of double bonds [1,2,6]. Experiments showed, however, that in the present case no isomerization occurs. Acid (I) with 1,4-structure is obtained. The substance obtained differs markedly from the possible product of isomerization (a 1,3-dienoic acid) in melting point ($\Delta^{1,3}$-dihydrobenzoic acid has m.p. 94-95°) [7]. The absence of an isomeric transformation is evidently associated with the fact that the carboxyl group activates the hydrogen in the 3-position to a lesser extent than the carbonyl group; migration of the double bond is bound up with ionization of the hydrogen.

Condensation of propiolic acid with piperylene could be expected to lead to formation of two isomeric acids with different positions of the methyl and carboxyl groups.



The acid actually obtained (II) gave o-toluic acid on dehydrogenation over sulfur, and also after successive halogenation and dehalogenation; on oxidation with dilute HNO_3 under pressure at 180-200° it gave o-phthalic acid. Consequently, the reaction only goes in accordance with the rule previously established for reactions of piperylene – the substituent in the conjugated system and the carboxyl group are in the ortho-position [8-10].

There is likewise no doubt about the position of the double bonds in the acid obtained. Acid (II) differs markedly in melting point from its possible isomers with conjugated systems of double bonds ($\Delta^{1,5}$-, $\Delta^{2,6}$- and $\Delta^{4,6}$-dihydrobenzoic acids melt at 76-78° [11], 175° [12] and 128° [13], respectively). It did not react with maleic anhydride.

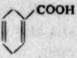
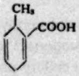
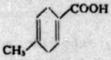
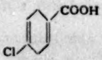
Condensation of piperylene with methyl propiolate gave the methyl ester of acid (II). Hydrolytic cleavage yielded acid (I), identical in properties with the preparation described above.

Condensation of propiolic acid and its methyl ester with isoprene gave $\Delta^{1,4}$-dihydro-p-toluic acid (III) and its methyl ester. Dehydrogenation of this acid over Pd gave p-toluic acid, oxidation of which with dilute nitric acid gave terephthalic acid. Acid (III) did not react with maleic anhydride and therefore did not contain a conjugated system of double bonds. The dihydro-p-toluic acids have not been described in the literature.

Propiolic acid and 2-chlorobutadiene-1,3 gave 4-chloro-$\Delta^{1,4}$-dihydrobenzoic acid (IV). Oxidation with dilute HNO_3 converted the latter into p-chlorobenzoic acid.

Heating of propiolic acid with cyclohexadiene-1,3 led to cleavage of the endoethylenic bridge from the primary product of condensation: benzoic acid and ethylene were formed. A similar process was observed on condensation of cyclohexadiene with propargyl aldehyde and butynone [1,2].

The constants of the acids and methyl esters that we prepared are shown in the table below.

Acid		Melting point	Constants of the methyl ester				
			Boiling point at 20 mm	d_4^{20}	n_D^{20}	MR	
						found	calculated
(I)		121°	94—95.5°	1.0720	1.4938	37.37	37.67
(II)		85—86	88—90	1.0269	1.4871	42.63	42.28
(III)		180—181	110.5—111.5	1.0435	1.4930	42.38	42.28
(IV)		216—217	—	—	—	—	—

We see from the table that the presence of a methyl group in the ring increases the polarizability of the molecules: the molecular refraction found is slightly higher than the calculated value.

The present investigation showed that propiolic acid, like other acetylenic dienophiles, condenses with dienic hydrocarbons and their derivatives in a manner depending upon the electronic polarization of the combining molecules. In no instance was the second possible isomer detected. It is evident that even if it is formed, its amount is extremely small, and it cannot be isolated when working with small amounts of the substances.

EXPERIMENTAL

Condensation of butadiene with propiolic acid. 3 g propiolic acid and 6 ml butadiene in 10 ml toluene (0.1 g hydroquinone) were heated in sealed glass tubes at 145-150° for 10 hours. Crystals of acid (I) separated out when the tubes were cooled. Yield 4.7 g (88%).

Found %: C 68.21, 68.04; H 6.55, 6.38. Equiv. 123.6, 123.7. $C_7H_8O_2$. Calculated %: C 67.73; H 6.49. Equiv. 124.1.

A solution of 0.5 g acid (I) and 0.5 g maleic anhydride in 7 ml toluene was heated on a boiling water bath for 6 hours. After addition of 10 ml 10% KOH solution, the liquid was boiled for 1½ hours and the aqueous layer was separated and acidified. 0.47 g substance was obtained with melting point (from benzene) 119-120° not giving a depression in admixture with the original acid (I).

0.5 g acid (I) was mixed with 1.5 g sulfur and heated under an air condenser for 45 minutes. The reaction product melted at 118-119° after purification by sublimation. A mixed sample with the original acid (I) melted at 99-101°. A mixed sample with benzoic acid did not give a depression of melting point.

0.2 g bromine in 2 ml chloroform was added, with cooling, to a solution of 0.2 g acid in 15 ml chloroform. Removal of the solvent in vacuum left a crystalline product (0.4 g) which was recrystallized from benzene. M.p. 151-152°.

Condensation of butadiene with methyl propiolate. 6.5 g methyl propiolate, 10 ml butadiene, 15 ml toluene and 0.1 g hydroquinone were heated in sealed tubes at 120° for 6 hours. Fractionation of the reaction mixture in vacuum gave 7.2 g (70%) of condensation product.

The constants of this and the other substances are given in the table.

Found %: C 69.43, 69.35; H 7.44, 7.69. $C_8H_{10}O_2$. Calculated %: C 69.54; H 7.29.

0.3 g of the ester was boiled with 1.5 ml 10% sodium hydroxide solution for 1½ hours. Acidification of the solution resulted in separation of crystals (0.22 g) with m.p. 120-121° (from benzene). A mixed sample with acid (I) melted at the same temperature.

Condensation of piperylene with propiolic acid. 4.8 g propiolic acid, 13 ml piperylene, 10 ml toluene and 0.1 g hydroquinone were heated in sealed tubes at 120° for 12 hours. After driving off the toluene in vacuum, the residue rapidly crystallized. Yield 7 g (74%). Acid (II) was recrystallized from gasoline (60-70° fraction).

Found %: C 70.01, 69.97; H 7.47, 7.70. $C_8H_{10}O_2$. Calculated %: C 69.54; H 7.29.

After heating 0.5 g acid (II) with maleic anhydride under the conditions described above, the original acid with m.p. 84° was recovered. A mixed test with the authentic acid (II) did not give a depression.

0.5 g acid (II) was mixed with 1.5 g sulfur and heated for 1 hour. A substance with m.p. 101-102° (from hot water) sublimed. A mixed test with the original acid melted at 74-77°.

0.2 g acid was heated in a sealed tube with 20% HNO_3 for 10 hours at 180-200°. o-Phthalic acid with m.p. 189-191° was extracted from the resultant solution. The identity of the acid was confirmed by conversion to fluorescein. Isophthalic acid was not detected.

Condensation of piperylene with methyl propiolate. 3.2 g methyl propiolate, 6.4 g piperylene and 0.1 g hydroquinone in 10 ml toluene were heated in sealed tubes at 140-145° for 10 hours. Yield of condensation product 4.05 g (71%).

Found %: C 70.88, 71.23; H 8.21, 8.29. $C_9H_{12}O_2$. Calculated %: C 71.03; H 7.95.

A mixture of 0.5 g of the substance and 2.5 ml 10% NaOH was boiled for 1 hour and then acidified. Acid (II) with m.p. 85-86° (from gasoline) was extracted from the resultant solution with chloroform. A mixed test with acid (II) obtained in the preceding experiment did not give a depression.

Condensation of isoprene with propiolic acid. 3.5 g propiolic acid, 3.5 g isoprene and 0.1 g hydroquinone in 12 ml toluene were heated in sealed tubes at 145-150° for 10 hours. Crystals of acid (III) came out on cooling. Yield 4.9 g (70%). The acid was recrystallized from benzene.

Found %: C 69.72, 69.79; H 7.72, 7.18. Equiv. 137.7. $C_8H_{10}O_2$. Calculated %: C 69.54; H 7.29. Equiv. 138.2.

The acid was recovered unchanged after heating with maleic anhydride.

0.14 g acid (III), 0.45 g maleic anhydride and 0.2 g palladium black in 10 ml water were boiled for 6 hours. The hot-filtered solution deposited crystals of p-toluic acid (m.p. 180-181°) after cooling. A mixed test with authentic p-toluic acid melted at 179°. *

Oxidation of 0.15 g acid (III) with dilute nitric acid at 150-155° for 10 hours gave terephthalic acid. The dimethyl ester melted at 136-140°.

To 1.5 g acid (III) in 6.5 ml methyl alcohol was added a few drops of H_2SO_4, and the mixture boiled on a water bath for 4 hours. After dilution of the mixture, the products of reaction were extracted with ether. The ethereal extract was washed with sodium carbonate solution and with $CaCl_2$ and distilled to give 1.45 g methyl ester of acid (III).

B.p. 110.5° (20 mm), d_4^{20} 1.0430, n_D^{20} 1.4920.

Condensation of isoprene with methyl propiolate. 6.0 g methyl propiolate, 7 ml isoprene and 0.1 g hydroquinone in 20 ml toluene were heated at 140-145° for 10 hours. Fractional distillation of the reaction products in vacuum gave 8.0 g (73%) methyl ester of acid (III).

Found %: C 70.84; H 8.31; OCH_3 19.85. $C_9H_{12}O_2$. Calculated %: C 71.03; H 7.95; OCH_3 20.39.

A solution of 0.5 g of the ester in 2.5 ml 10% NaOH solution was boiled for 1 hour. After acidification, acid (III) with m.p. 179° (from benzene) came down. A mixed melting test with the acid (III), described in the preceding experiment, did not give a depression.

An attempt to hydrogenate the ester over colloidal Pd was unsuccessful. During this treatment the ester is evidently transformed into a mixture of aromatic and completely hydrogenated substances. Hydrolysis of this mixture gave a mixture of acids melting at 100-130°.

Hydrogenation of 1.03 g of the ester in presence of Raney nickel resulted in addition of 277 ml hydrogen (18.5°, 763 mm) after 10 hours, instead of the calculated amount of 280.4.

Condensation of cyclohexadiene with propiolic acid. 5 g propiolic acid, 9 g cyclohexadiene and 0.1 g hydroquinone in 15 ml toluene were heated at 115-120° in sealed tubes for 7 hours. The tubes were cooled with freezing mixture before opening. Release of ethylene was observed on opening. After removal of the solvent, the crystalline precipitate was recrystallized from water. M.p. 119°. A mixed melting test with benzoic acid did not give a depression. Yield of benzoic acid 3.5 g (40%).

Condensation of 2-chlorobutadiene with propiolic acid. 3.7 g propiolic acid, 4.2 g 2-chlorobutadiene and 0.1 g hydroquinone in 15 ml toluene were heated for 12 hours at 115-120°. Crystals came down when the tubes were opened. Yield 6.1 g (72%). They were recrystallized from toluene.

Found %: Cl 22.29. $C_7H_7O_2Cl$. Calculated %: Cl 22.36.

0.1 g acid was heated in a sealed tube with dilute HNO_3 at 150-155° for 10 hours. The crystals that separated were identified as p-chlorobenzoic acid. M.p. 242° (from water). The literature [14] gives m.p. 243°.

SUMMARY

1. The condensation of butadiene, piperylene, isoprene, cyclohexadiene and 2-chlorobutadiene with propiolic acid and its methyl ester was investigated.

2. In all cases, except that of the condensation with cyclohexadiene, the reaction leads to $\Delta^{1,4}$-dihydrobenzoic acids and their methyl esters.

3. The structure of the acids obtained was confirmed by transformation into the corresponding aromatic mono- and dibasic acids.

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*p-Dihydrotoluic acid does not give a depression of melting point in a mixed test with p-toluic acid. Transition of the dihydrotoluic acid into p-toluic acid may possibly occur near the melting point.

4. Heating of propiolic acid with cyclohexadiene gives benzoic acid and ethylene.

5. It was established that in the condensation of dienic hydrocarbons with propiolic acid and ester, the course of the condensation is governed by the electronic polarization of the components.

LITERATURE CITED

[1] A. A. Petrov, Proc. Acad. Sci. USSR 53, 531 (1946); J. Gen. Chem. 17, 497 (1947); 24, 2136 (1954).

[2] A. A. Petrov and N. P. Sopov, J. Gen. Chem. 17, 1295 (1947); 22, 890 (1952) (T.p. 949);• 23, 1034 (1953) (T.p. 1085);• 25, 517 (1955) (T.p. 485);• Proc. Acad. Sci. USSR 79, 811 (1951).

[3] K. Alder, G. Stein and S. Schneider, Ann. 525, 183 (1936).

[4] E. Dane, O. Höss and K. Eder, Ann. 536, 183 (1938).

[5] K. Alder and K. H. Backendorf, Ber. 71, 2199 (1938).

[6] J. C. Lunt and F. Sondheimer, J. Chem. Soc. 1950, 3361.

[7] A. Eichnegrün and A. Einhorn, Ber. 23, 2886 (1890); 26, 454 (1893).

[8] A. A. Petrov and A. F. Sapozhnikova, J. Gen. Chem. 18, 424 (1948).

[9] A. A. Petrov, J. Gen. Chem. 18, 1125 (1948).

[10] A. A. Petrov and N. P. Sopov, J. Gen. Chem. 22, 591 (1952) (T.p. 653);• 24, 298 (1954) (T.p. 299).•

[11] A. J. Birch, J. Chem. Soc. 1950, 1551.

[12] F. P. Mazza and A. Calo, Gazz.chim. ital. 57, 315 (1927).

[13] W. H. Perkin, J. Chem. Soc. 99, 758 (1911).

[14] Dictionary Organic Compounds (Foreign Lit. Press, 1949).

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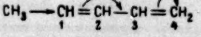
CONJUGATED SYSTEMS

LXIII. THE ACTION OF BENZENESULFODICHLORAMIDE ON ALCOHOLIC SOLUTIONS OF PIPERYLENE

T. A. Zyryanova and A. A. Petrov

In previous communications in this series it was shown that butadiene adds on hypohalous acids and their esters predominantly in the 1,2-position when its aqueous or alcoholic solutions are treated with benzenesulfodichloramide [1]. It was desirable to compare these results with data for the direction of addition under the same conditions of hypohalous compounds to homologs of butadiene. The present communication deals with the direction of addition of alkyl hypochlorites to piperylene.

Piperylene differs from butadiene in having a high polarity (dipole moment 0.68) [2]. It was to be expected that this property would strongly influence the orienting effect of components in the addition to piperylene of halogens, hydrogen halides and hypohalites. Reactions of this type have been studied very incompletely in the case of piperylene. It is merely known that piperylene adds on bromine [3] and hydrogen bromide [4], predominantly in the 1,4-position; in the latter case the hydrogen atom combines at the fourth carbon atom of the diene system:



The following 6 unsaturated ethers may be expected to result from the action of benzenesulfodichloroamide on a solution of piperylene in methanol:

$$CH_3-CH=CH-CHOCH_3-CH_2Cl; \quad \text{(I)}$$

$$CH_3-CH=CH-CHCl-CH_2OCH_3; \quad \text{(II)}$$

$$CH_3-CHCl-CHOCH_3-CH=CH_2; \quad \text{(III)}$$

$$CH_3-CHOCH_3-CHCl-CH=CH_2; \quad \text{(IV)}$$

$$CH_3-CHOCH_3-CH=CH-CH_2Cl; \quad \text{(V)}$$

$$CH_3-CHCl-CH=CH-CH_2OCH_3. \quad \text{(VI)}$$

Actually a product was obtained with a fairly narrow boiling range (5°), although the study of its properties convinced us that we were dealing with a mixture of at least two isomeric chloroethers.

The structure of these isomers was established in the following manner.*

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*The usual methods of determination of structure that we applied enabled us to detect isomeric substances in amounts greater than 5-10%.

1. Ozonization of the substance under the usual conditions followed by oxidation of the products of decomposition of the ozonides with potassium permanganate gave acetic and chloroacetic acids. Formaldehyde and formic acid were not present in the oxidation products to any appreciable extent. The absence of chloroethers (II) and (IV) from the mixture was thus proved.

Acetic acid could be formed from chloroethers (I) and (II), but chloroacetic acid could only be formed from chloroether (V). Since later experiments showed that isomer (II) was absent, the acetic acid must have been derived from (I).

2. Treatment of the original mixture of isomers with alcoholic alkali gave two substances: the enol ether (VII) and the dimethyl ether of an unsaturated glycol, evidently (VIII), in 4:3 molar ratio.

The structure of the first substance was established by conversion to methyl propenyl ketone (by short-period treatment with 5% H_2SO_4 in the cold). The ketone was identified by its constants and the melting point of its 2,4-dinitrophenylhydrazone.

Formation of enolic ethers from substances (II), (IV), (V) and (VI) is extremely improbable since they all contain allylic chlorine which is easily substituted by the action of alcoholic alkali on the alkoxyl.*

An unsaturated ether of enolic character might be obtained from chloroether (III), but on hydrolysis it could only form ethyl vinyl ketone, which differs from methyl propenyl ketone in boiling point (more than 20° difference) [5].

Consequently the enolic ether (VII) is evidently formed from chloroether (I) and the latter must therefore be regarded as the principal component of the reaction mixture.

The dimethyl ether of the pentenediol (VIII) could be formed by the action of alcoholic alkali on chloroethers (II), (IV), (V) and (VI) [in the case of (II) and (IV) in consequence of an allyl rearrangement]. Since the absence from the mixture of chloroether (IV) had previously been demonstrated, and the absence of (II) and (VI) was shown in the subsequent separation, the dimethyl ether (VIII) is evidently the result of reaction of chloroether (V) with alcoholic alkali.

Hydrogenation of the dimethyl ether of pentenediol over colloidal Pd gave the dimethyl ether of pentanediol-1,4.

Judging by the amount of the two products of the reaction of the mixture of chloroethers with alcoholic alkali, chloroether (I) forms 55-60% of the total reaction product. The remainder is chloroether (V).

3. Hydrogenation of the mixture of chloroethers over Raney nickel under pressure at room temperature gave, in 2:3 molar ratio, the following: 1) a mixture of methyl ethers of secondary amyl alcohol (IX) and methyl propenyl carbinol (X), and 2) a mixture of the methyl ether of 1-chloropentanol-2 (XI) and chloroether (I).

Supplementary hydrogenation of the mixture of (IX) and (X) over colloidal Pd gave pure (IX). The structure of the compound was confirmed by comparison of its properties with those of authentic (IX) obtained by alkylation of secondary amyl alcohol with methyl iodide.

Formation of (IX) is possible on hydrogenation of chloroethers (I), (IV) and (V). As already noted, isomer (IV) is absent from the original mixture (ozonization data). Special experiments demonstrated the nonsusceptibility of (I) and (IX) to reduction under selected conditions with loss of chlorine. Consequently ethers (IX) and (X) could be obtained by hydrogenation of chloroether (V).

Supplementary hydrogenation of the mixture of chloroethers (I) and (XI) over Raney nickel yielded the pure saturated chloroether (XI). In another experiment, chloroether (XI) was freed from (I) by bromination. Heating of (XI) with a solution of KOH in "cellosolve" or in methyl alochol in sealed tubes at 120° gave the methyl ether of the enolic form of methyl propyl ketone (XII). Treatment with 5% H_2SO_4 in the cold converted

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*If the possibility is assumed of formation from chloroethers (II), (IV), (V) and (VI) (as a result of dehalogenation and hydrolysis) of carbonyl compounds, then the results of this experiment exclude the presence of only chloroethers (II), (III) and (VI); (II) and (VI) must also give aldehyde. Chloroethers (IV) and (V) might give methyl propenyl ketone as a result of isomerization of the initally formed methyl allyl ketone. The absence of (IV), however, was demonstrated by ozonization, while such a course of the reactions is extremely improbable in the case of (V).

(XII) into methyl propyl ketone. Ozonization of (XII) gave formaldehyde and butyric acid. These transformations show that the methoxyl group in (XII) is at the third carbon atom of the diene system, and that the double bond is between the 3rd and 4th carbon atoms.

Chloroether (XI) and enol ether (XII) could have been formed only from the unsaturated chloroether (I). Thus the results of hydrogenation are likewise consistent with the view that chloroether (I) is the main product of addition of methyl hypochlorite to piperylene.

The hydrogenation experiments led us to the conclusion that the primary chloroethers (II) and (VI) are absent from the reaction mixture, since these ethers could on hydrogenation only give the methyl ether of primary amyl alcohol whose boiling point is 10° different from that of the ether that we isolated.

The structure of the products of addition of ethyl hypochlorite to piperylene was similarly verified. It should be noted that in this case the decomposition of the ozonide, after standing for some considerable time, is accompanied by the formation in a secondary reaction of a small quantity of formaldehyde.

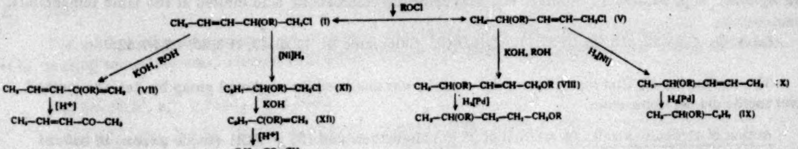
It should also be noted that treatment of piperylene in alcoholic solutions (especially methanol) with benzenesulfodichloroamide results to some extent in chlorination of the piperylene with substitution of hydrogen. due to which a small initial fraction appears in the reaction products. This phenomenon is not unexpected since the susceptibility of piperylene to substitution reactions is well known [3].

The present investigation has revealed much higher yields of 1,4-products in addition reactions of alkyl hypochlorites and piperylene than in the case of butadiene. Consequently the higher polarity of the dienic system under the influence of the radical in the 1-position facilitates 1,4-addition.

In the case of 1-chloro- and 1-bromobutadienes-1,3, the polarization of the dienic system is similarly increased, but this is due to another mechanism and 1,4-addition is not facilitated [6]. This difference in the orienting effect of halogen and alkyl group is evidently associated with deactivating substitution of the double bond under the influence of the inductive effect of the halogen atom. A part may also be played by the steric hindrance developed by addition of a group in the 1-position where there is already a large electronegative substituent (a halogen atom).

Also of outstanding interest is the fact that, although piperylene also gives two addition products, both contain the chlorine in the 4-position. In dienic syntheses piperylene likewise manifests a strict orientation in conformity with the direction of polarization of its molecule: ortho-substituted hydroaromatic compounds are formed [7].

The transformations discussed above are shown in the following scheme:


$CH_3-CH=CH-CH=CH_2$
ROCl
$CH_3-CH=CH-CH(OR)-CH_2Cl$ (I)
$CH_3-CH(OR)-CH=CH-CH_2Cl$ (V)
KOH, ROH
[Ni]H$_2$
KOH, ROH
H$_2$[Ni]
$CH_3-CH=CH-C(OR)=CH_2$ (VII)
[H+]
$CH_3-CH=CH-CO-CH_3$
$C_3H_7-CH(OR)-CH_2Cl$ (XI)
KOH
$C_3H_7-C(OR)=CH_2$ (XII)
[H+]
$C_3H_7-CO-CH_3$
$CH_3-CH(OR)-CH=CH-CH_2OR$ (VIII)
H$_2$[Pd]
$CH_3-CH(OR)-CH_2-CH_2-CH_2OR$
$CH_3-CH(OR)-CH=CH-CH_3$ (X)
H$_2$[Pd]
$CH_3-CH(OR)-C_3H_7$ (IX)

EXPERIMENTAL

Action of Benzenesulfodichloroamide on a Solution of Piperylene in Methyl Alcohol

The piperylene used in the work had m.p. 41.9-43°, d_4^{20} 0.6796, n_D^{20} 1.4320, and contained about 70-75% of trans-isomer.

Dichloroamide (135 g) was added in small portions over 3-4 hours to a solution of 135 g (200 ml) piperylene (60% excess) in 600 ml methyl alcohol with mechanical stirring and cooling to 0-5°. The mixture was thereupon allowed to stand until the active chlorine had almost completely disappeared, after which it was distilled with steam. A small quantity of sodium sulfite was added to the flask prior to distillation. The distillate was diluted with saturated $CaCl_2$ solution, and the oil was collected, washed with $CaCl_2$ solution and dried over calcined $CaCl_2$. The piperylene (excess) was then distilled off at the normal pressure, and the residue was distilled in vacuum (20 mm) in a 50 cm Widmer column. The following fractions were collected: 1) 20-40°, 5 g; 2) 40-50°, 4 g; 3) 50-55°, 5.5 g; 4) 55-60°, 77.2 g; residue 6.6 g.

Distillation of the 1st fraction at the ordinary pressure gave about 2 g of substance with b.p. 106-107°, d_4^{20} 0.9332, n_D^{20} 1.4690. Analysis showed the substance to be impure chloropentadiene.

Found %: Cl 30.07, 30.19; OCH_3 4.20. C_5H_7Cl. Calculated %: Cl 34.57.

In one experiment 60 g main (4th) fraction was redistilled in the same column to give 4.7 g of 55-58° fraction and 39.1 g 58-60° (20 mm) fraction.

55-58° fraction: d_4^{20} 0.9784, n_D^{20} 1.4431.

Found %: Cl 26.36, 26.00; OCH_3 22.48, 22.50. $C_5H_8OCH_3Cl$. Calculated %: Cl 26.34; OCH_3 23.05.

58-60° (20 mm) fraction: d_4^{20} 0.9856, n_D^{20} 1.4451.

Found %: Cl 26.03, 26.27; OCH_3 23.70. $C_5H_8OCH_3Cl$. Calculated %: Cl 26.34; OCH_3 23.05.

Since both fractions had substantially the same analysis and were fairly pure chloroethers with the proposed gross formula, they were worked up together in the subsequent operations.

Ozonization. 10.6 g substance was taken for ozonization. The ozonide in a sample was tested for formaldehyde with the help of β-naphthol [8]; none was detected. After decomposition of the main mass of ozonides with water, the aldehydes were oxidized with potassium permanganate until rapid decolorization ceased. 17.5 g permanganate was consumed. After the mixture had been freed from manganese dioxide (with the help of SO_2) and acidified, the acid was extracted with ether in a mechanical extractor. By the usual method about 2 g acetic acid with b.p. 50-60° (100 mm) and 3.4 g substance with b.p. about 90° (10 mm) were isolated from the ethereal solution. The greater part of the latter substance crystallized.

The acetic acid was converted to the silver salt which was analyzed.

Found %: Ag 64.67. $C_2H_3O_2Ag$. Calculated %: Ag 64.63.

The crystals coming out of the second fraction were collected (weight 1.5 g) and twice recrystallized from ligroine. M.p. 64.5-66.5°. A mixed test with authentic chloroacetic acid melted at the same temperature.

Found %: C 25.52; H 3.29; Cl 37.77. $C_2H_3O_2Cl$. Calculated %: C 25.42; H 3.20; Cl 37.52.

The mother liquor, after separation of the crystals, was analyzed for methoxyl group by Zeisel's method. Silver iodide did not come down.

Action of alcoholic alkali. A solution of 95 g chloroethers and 128 g KOH (triple excess) in 340 ml methanol was boiled for 18 hours on a water bath. After dilution of the distillate with water, the reaction products were distilled with water and alcohol and salted out from the distillate with $CaCl_2$. They were then washed again with saturated $CaCl_2$ solution; the residue was extracted with ether. From the ethereal extract, after washing with saturated $CaCl_2$ solution, an additional amount of reaction products could be extracted. In all 42.5 g oil was obtained, which in a first distillation (in a Widmer column) at 100 mm gave two fractions: 1) up to 60°, 17.7 g; 2) 60-90° (mostly 85-90°), 17.9 g.

On redistillation of the 1st fraction at normal pressure, the greater part came over at 105-107°. The ether (VII) had d_4^{20} 0.8350, n_D^{20} 1.4535.

Found %: C 73.92; H 10.73; OCH_3 31.61, 31.96. $C_5H_7OCH_3$. Calculated %: C 73.42; H 10.27; OCH_3 31.62.

On shaking 5 g of ether (VII) with 50 ml 5% H_2SO_4, it quickly dissolved (over 95%). Methyl propenyl ketone with b.p. 120-121°, n_D^{20} 1.4352, was separated from the solution with saturated ammonium sulfate. Its 2,4-dinitrophenylhydrazone melted (from alcohol) at 157-158°.

For methyl propenyl ketone the literature [9] gives: b.p. 122°, n_D^{20} 1.4350; 2,4-dinitrophenylhydrazone m.p. 157-158°.

Redistillation of the 2nd fraction at 20 mm gave the following fractions: 1st up to 52.5°, 1.5 g; 2nd 52.5-53.5°, 10 g; 3rd 53.5-54.5°, 3.3 g; residue 2 g.

Dimethyl ether (VIII):

B.p. 52.5-53.5° (20 mm), d_4^{20} 0.8882, n_D^{20} 1.4220, MR 37.25; calc. 37.35.

Found %: C 64.11; H 11.30; OCH_3 47.52, 47.80. $C_5H_8(OCH_3)_2$. Calculated %: C 64.58; H 10.84; OCH_3 37.68.

5 g (VIII) was hydrogenated over colloidal Pd (5 mg) in methyl alcohol. 997 ml H_2 was absorbed in the course of 4½ hours (18°, 769 mm). The calculated amount of H_2 is 970 ml (under normal conditions). The dimethyl ether of pentanediol was isolated from the solution by extraction with ether and salting out with $CaCl_2$.

B.p. 144.5-145°, d_4^{20} 0.8583, n_D^{20} 1.4050, MR 37.75; calc. 37.81.

Found %: C 63.67; H 11.89; OCH_3 46.98, 47.28; $C_5H_{10}(OCH_3)_2$. Calculated %: C 63.60; H 12.20; OCH_3 46.95.

Hydrogenation. 77 g original mixture of chloroethers was hydrogenated in solution in methanol (200 ml) in presence of Raney nickel (10 g paste) at 20° at an initial pressure of 50 atm in presence of 30 g $CaCO_3$ (to bind the HCl). The autoclave was then opened, 30 g sodium acetate and 10 g catalyst were added to the mixture, and hydrogenation was continued until hydrogen ceased to be absorbed. About 5 hours were spent on both operations.

The reaction mixture was diluted with water and the products distilled with steam and alcohol. The products were isolated from the distillate with saturated $CaCl_2$ solution. In this manner 50 g oil was obtained and was distilled in a 25 cm Widmer column to give: 1st fraction 87-95° (mainly 87-88°), 15 g; 2nd fraction 95-143°, 1.7 g; 3rd fraction 143-146°, 26.1 g; residue 4.6 g.

The first fraction almost entirely came over within an 0.5° range when redistilled. B.p. 88-88.5°, d_4^{20} 0.7601, n_D^{20} 1.3890.

For the methyl ether of methyl propenyl carbinol (X) the literature [4] gives: b.p. 88-89°, d_4^{20} 0.7663, n_D^{20} 1.3948.

The methyl ether of secondary amyl alcohol (IX) has not been described in the literature. We obtained it by treating secondary amyl alcohol with methyl iodide and KOH in sealed tubes on a boiling water bath.

B.p. 88-88.5°, d_4^{20} 0.7564, n_D^{20} 1.3840.

Found %: OCH_3 30.31, 30.51. $C_5H_{11}OCH_3$. Calculated %: OCH_3 30.37.

Since the specific gravity and refractive index of the ether that we isolated were intermediate between those of the saturated and unsaturated ethers, we concluded that it was a mixture of these ethers. Actually, the hydrogenation of 5 g of the substance in 50 ml methanol in presence of 5 mg Pd for 5 hours resulted in absorption of 416 ml H_2 (20°, 756 mm). The saturated ether isolated from solution had the constants:

B.p. 88-88.5°, d_4^{20} 0.7546, n_D^{20} 1.3840, MR 31.66; calc. 31.55.

Found %: C 70.90, 70.88; H 13.60, 13.65; OCH_3 30.20, 30.30. $C_5H_{11}OCH_3$. Calculated %: C 70.53; H 13.81; OCH_3 30.37.

The 3rd fraction (XI + I) had the constants:

B.p. 48-48.5° (20 mm), d_4^{20} 0.9653, n_D^{20} 1.4263.

Found %: Cl 26.21, 25.90; OCH_3 22.51, 22.60. $C_5H_{10}OCH_3Cl$. Calculated %: Cl 26.00; OCH_3 22.71. $C_5H_8OCH_3Cl$. Calculated %: Cl 26.34; OCH_3 23.05.

8 g of mixture of ethers (XI + I) in 200 ml methyl alcohol was hydrogenated in presence of 15 g Raney nickel (paste) at an initial pressure of 70 atm for 4 hours. After working up in the manner described above, no ethers containing chlorine could be detected. The first drops of distillate appeared at 140°. The saturated chloroether (XI) had the constants:

B.p. 143-144°, 48-48.5° (20 mm), d_4^{20} 0.9590, n_D^{20} 1.4250, MR 36.43. $C_6H_{13}OCl$. Calc. 36.42.

The substance does not react with bromine.

In another experiment 4.3 g mixture of (XI) and (I) was treated with a chloroform solution of bromine. 0.715 g bromine was consumed, corresponding to a 14% content of (I). The chloroether (XI), separated from chloroform and products of bromination, had the constants:

B.p. 48-48.5° (20 mm), d_4^{20} 0.9639, n_D^{20} 1.4260.

Found %: Cl 26.19, 26.41; OCH_3 22.51, 22.60. $C_5H_{10}OCH_3Cl$. Calculated %: Cl 26.00; OCH_3 22.71.

14 g chloroether (XI) was refluxed for 4 hours with a solution of 18 g KOH in 100 ml "cellosolve." The reaction products were distilled after dilution of the distillate with water. By salting-out treatment, the fresh distillate yielded 4.2 g oil, a large part of which came over in a Widmer column at 89-90°. The residue was unreacted (XI). The same substance was obtained by heating (XI) with excess KOH in methyl alcohol at 120° in sealed tubes.

2-Methoxypentene-1 (XII) has the constants:

B.p. 89-90°, d_4^{20} 0.7888, n_D^{20} 1.4062, MR 31.15; calc. 31.08.

Found %: C 72.12; H 11.97; OCH_3 30.99, 31.06. $C_5H_9OCH_3$. Calculated %: C 71.95; H 12.08; OCH_3 30.98.

The substance dissolved when 1.4 g (XII) was shaken with 50 ml 5% H_2SO_4. Salting-out with potassium carbonate and distillation from the solution gave 0.8 g methyl propyl ketone with b.p. 100.5-102.5°, d_4^{20} 0.8087, n_D^{20} 1.3910. The ketone gave a 2,4-dinitrophenylhydrazone, m.p. 141° (from alcohol).

Literature data [5]: b.p. 102°, d_4^{20} 0.8089, n_D^{20} 1.3895. 2,4-Dinitrophenylhydrazone, m.p. 141°.

Found %: N 21.13. $C_{11}H_{14}O_4N_4$. Calculated %: N 21.04.

0.7489 g substance (XII) was ozonized. From a one-fifth portion of ozonide was obtained 0.1574 g dinaphtholmethane. Butyric acid was detected in the products of decomposition of the remaining portion of ozonides. It was identified by odor and by analysis of the silver salt.

Found %: Ag 54.15. $C_4H_7O_2Ag$. Calculated %: Ag 54.07.

Action of Benzenesulfodichloroamide on a Solution of Piperylene in Ethyl Alcohol

Under the conditions described in the preceding section, 68 g piperylene in 200 ml ethyl alcohol and 67.5 g benzenesulfodichloroamide gave 56.6 g oil. 17.5 g piperylene was recovered.

Fractional distillation of the oil at 20 mm gave the following fractions: 1st up to 56°, 3.4 g, n_D^{20} 1.4720; 2nd 56-61°, 7.6 g; 3rd 61-64°, 30.8 g; 4th 64-66°, 3.2 g (n_D^{20} 1.4438); residue 4.4 g.

Fraction 56-61° at 20 mm: d_4^{20} 0.9576, n_D^{20} 1.4390.

Found %: Cl 24.32, 24.26; OC_2H_5 30.70. $C_5H_8OC_2H_5Cl$. Calculated %: Cl 23.86; OC_2H_5 30.32.

Fraction 61-64° at 20 mm: d_4^{20} 0.9613, n_D^{20} 1.4427.

Found %: Cl 24.31, 23.98; OC_2H_5 30.40, 30.50. $C_5H_8OC_2H_5Cl$. Calculated %: Cl 23.86; OC_2H_5 30.32.

The 2nd and 3rd fractions were worked up together for determination of composition.

Ozonization. Cleavage of the ozonides from 11.2 g substance gave acetic and chloroacetic acids. Acetic acid was determined as the silver salt.

Found %: Ag 64.80, 64.41. $C_2H_3O_2Ag$. Calculated %: Ag 64.63.

The chlorine content of the chloroacetic acid was determined.

Found %: Cl 37.44. $C_2H_3O_2Cl$. Calculated %: Cl 37.52.

The acid melted at 62-63.5° (from ligroine). A mixed test with authentic chloroacetic acid gave the same melting point. The residue from the crystals of chloroacetic acid did not conatin ethoxyls.

Formaldehyde was not detected in the products of cleavage of the freshly prepared ozonide. A small amount of formaldehyde was found in ozonide which had been kept for 24-48 hours.

Action of alcoholic alkali. 90 g of the mixture of chloroethers was boiled on a water bath for 18 hours with a threefold excess of KOH in 250 ml ethyl alcohol. 40 g oil was obtained which gave two fractions on distillation: 1st 120-130° at ordinary pressure, 17.7 g; 2nd 70-80° at 20 mm, 18.2 g.

When the 1st fraction was redistilled, the greater part came over at 124-126° and had d_4^{20} 0.8294 and n_D^{20} 1.4500.

Found %: C 74.73; H 10.51; OC_2H_5 40.10. $C_5H_7OC_2H_5$. Calculated %: C 74.95; H 10.78; OC_2H_5 40.17.

On shaking with 5% H_2SO_4, 2-ethoxypentadiene-1,3 dissolved and formed methyl propenyl ketone; 2,4-dinitrophenylhydrazone, m.p. 156-157°.

Refractionation of the 2nd fraction at 20 mm gave the following fractions: 1st, up to 72°, 5.5 g; 2nd, 72-75°, 2.5 g, (n_D^{20} 1.4253); 3rd, 75-77°, 11.0 g; residue, 2.8 g.

A further 9.3 g substance was isolated from the 75-77° fraction at 20 mm:

B.p. 76.5-77° (20 mm), d_4^{20} 0.8564, n_D^{20} 1.4235, MR 47.10; calc. 46.58.

Found %: C 68.62; H 11.60; OC_2H_5 56.51, 56.76. $C_5H_8(OC_2H_5)_2$. Calculated %: C 68.31; H 11.47; OC_2H_5 56.95.

Hydrogenation of the substance over colloidal palladium in methanol gave the diethyl ether of pentanediol:

B.p. 73-75° (20 mm), d_4^{20} 0.8511, n_D^{20} 1.4102.

Found %: C 67.11; H 12.39; OC_2H_5 56.09. $C_5H_{10}(OC_2H_5)_2$. Calculated %: C 67.45; H 12.58; OC_2H_5 56.24.

Hydrogenation. 74 g chloroethers in 200 ml methyl alcohol was hydrogenated in an autoclave in presence of 8 g Raney nickel (paste) at an initial pressure of 120 atm until H_2 ceased to be absorbed. The HCl was bound by adding 120 g sodium acetate to the autoclave. After working up in the usual manner, two fractions in 3:4 ratio were isolated.

1) Mixture of ethyl ethers of secondary amyl alcohol and methyl propenyl carbinol (13 g). The main fraction of this mixture had b.p. 106-107°, d_4^{20} 0.7741, n_D^{20} 1.4020.

According to the literature [4], the ethyl ether of methyl propenyl carbinol has the constants: b.p. 105-106°, d_4^{20} 0.7909, n_D^{20} 1.4042.

The following constants were found for the ethyl ether of secondary amyl alcohol, obtained by alkylation of this alcohol with ethyl iodide: b.p. 106-107°, d_4^{20} 0.7565, n_D^{20} 1.3880.

The mixture of these two ethers that we obtained was hydrogenated over colloidal Pd. 4.3 g substance absorbed 863 ml H_2 (22°, 750 mm).

The product of hydrogenation had the constants:

B.p. 105-106°, d_4^{20} 0.7536, n_D^{20} 1.3880.

Found %: C 71.97; H 13.53; OC_2H_5 38.68. $C_5H_{11}OC_2H_5$. Calculated %: C 72.35; H 13.87; OC_2H_5 38.77.

2) A mixture of the ethyl ether of 1-chloropentanol-2 and original substance (3,4-isomer) with b.p. 60-61° (20 mm), d_4^{20} 0.9510, n_D^{20} 1.4377.

Found %: Cl 23.34, 23.56. $C_7H_{15}OCl$. Calculated %: Cl 23.96.

This mixture was further hydrogenated over Raney nickel, and then had the constants: b.p. 60-61°, d_4^{20} 0.9319, n_D^{20} 1.4235. Bromination consumed an amount of bromine equivalent to 11% of the content of unsaturated chloroether. After separation from the products of bromination, the saturated chloroether had:

B.p. 60-60.5° (20 mm), d_4^{20} 0.9359, n_D^{20} 1.4230, MR 40.99; calc. 41.36.

Found %: Cl 23.50; OC_2H_5 29.78. $C_5H_{10}OC_2H_5Cl$. Calculated %: Cl 23.53; OC_2H_5 29.91.

SUMMARY

1. The action of benzenesulfodichloroamide on solutions of piperylene in methyl and ethyl alcohols was examined.

2. It was shown that the reaction gives a mixture of 1-chloro-2-alkoxypentenes-3 (3,4-addition) and 1-chloro-4-alkoxypentenes-2 (1,4-addition) in the molar ratio of 5-6:4.

3. Alcoholic KOH acts on the above mixture to give the corresponding 2-alkoxypentadienes-1,3 (ethers of the enol form of methyl propenyl ketone) and the full ethers of pentene-2-diol-1,4.

4. Hydrogenation of the mixture of chloroethers over Raney nickel under pressure gave the ethers of secondary amyl alcohol and 1-chloropentanol-2.

5. Treatment of the methyl ether of 1-chloropentanol-2 with alcoholic potash gave the methyl ether of the enol form of methyl propyl ketone.

6. The investigation established that the polarization of the dienic system under the influence of the hydrocarbon radical in the 1-position leads in the case of addition of alkyl hypochlorites (chloroamide method) to a considerable increase in yield of 1,4-product, the halogen atom becoming attached at the 4th carbon atom of the dienic system.

LITERATURE CITED

[1] A. A. Petrov, Symposium, Problems of Chemical Kinetics and Reactivity (Acad. Sci. USSR Press, 1955).

[2] N. B. Hannay and C. P. Smyth, J. Am. Chem. Soc. 65, 1931 (1943).

[3] A. A. Petrov and M. L. Genusov, Progr. Chem. 24, 220 (1955).

[4] A. N. Pudovik and N. B. Sharipova, J. Gen. Chem. 25, 589 (1955) (T.p. 561).*

[5] Dictionary Organic Compounds (Foreign Lit. Press, 1949).

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*T.p. = C. B. Translation pagination.

[6] A. A. Petrov, J. Gen. Chem. 10, 1682, 1887 (1940); 15, 981 (1945).

[7] A. A. Petrov et al., J. Gen. Chem. 18, 424, 1125 (1948); 22, 591 (1952) (T.p. 653);* 24, 298 (1954); (t;p; 299);* 25, 517 (1955) (T.p. 485).*

[8] V. N. Reich and B. A. Feinberg, Methods of Technical Analysis (State Chem. Press, 1953), 175.

[9] E. R. H. Jones and M. C. Whiting, J. Chem. Soc. 1423 (1949).

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*T.p. = C. B. Translation pagination.

PREPARATION OF HYDROAROMATIC COMPOUNDS ON THE BASIS OF PRODUCTS OF THE DIENE SYNTHESIS

IV. THE ACTION OF ORGANOMAGNESIUM COMPOUNDS ON ESTERS OF CYCLOHEXENE-4-DICARBOXYLIC ACIDS

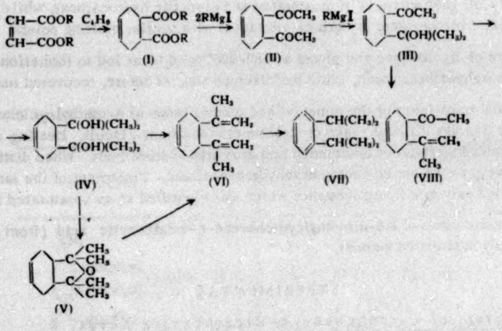
N. P. Sopov

In a series of earlier studies consideration was given to the problem of the possibility of obtaining hydroaromatic alcohols and hydrocarbons of the most diverse structures on the basis of products of cyclization of 1,3-dienic compounds with α,β-unsaturated carbonyl compounds, acids and their derivatives [1-3].

Continuing the investigations in this direction, we have studied the possibility of synthesis of hydroaromatic diketones and glycols from products of condensation of butadiene, piperylene, isoprene and dipropenyl with esters of maleic and fumaric acids.

This work contained several elements of interest. Firstly, it could lead to geometrically isomeric ketones, alcohols and hydrocarbons, and these in turn could serve as starting materials for further syntheses. Secondly, it was interesting to compare the properties of trienic (divinylcyclohexenic) hydrocarbons obtained by this route with the properties of vinylcyclohexadienic hydrocarbons described earlier [2].

The general scheme of these transformations is shown below (for butadiene):



Condensation of butadiene, piperylene, isoprene and dipropenyl with dimethyl and diethyl maleates and fumarates gave the corresponding esters of the isomeric Δ^4-tetrahydrophthalic acid and its homologs with different positions and numbers of methyl groups (I). Some of these substances were already described in a previous communication [4].

Reaction of geometrically isomeric dimethyl esters of cyclohexene-4-dicarboxylic acid (from butadiene) with 2.5 moles CH_3MgI gave the cis- and trans-forms of diketone (II). Both compounds crystallize. The trans-isomer has a considerably higher melting point.

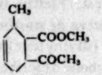
Crystalline derivatives of these diketones with hydrazine derivatives (semicarbazide, 4-nitro- and 2,4-dinitrophenylhydrazines) could not be isolated. During preparation of the cis-diketone, a liquid substance is formed. On the basis of analysis and a study of properties, the latter is assigned formula (VIII).

The following properties of the substance are consistent with formula (VIII): It does not evolve hydrogen when treated with Grignard reagent and is therefore not an alcohol. It does not isomerize when reacted with acids, and therefore cannot be a furan derivative. Consequently, the oxygen can only be in a carbonyl group.* The infrared spectrum of the substance exhibited absorption bands corresponding to the double carbon-carbon and carbonyl bonds.

Unsaturated ketone (VIII) is evidently formed by dehydration of ketoalcohol (III). Reaction of the isomeric ketones with 2.5-3 moles CH_3MgI (or 5 moles calculated on the original esters) gave crystalline glycols (IV). On distillation or heating with 10% oxalic acid, the cis-glycol readily dehydrates with formation of the corresponding hexahydrobenzofuran derivative (V). The trans-glycol does not react.

Heating of both glycols with acetic anhydride at 230-240° for 12 hours gave the corresponding aromatic hydrocarbons (VII) with a small admixture of unsaturated hydrocarbons. Consequently, dehydration is accompanied by isomerization. Treatment of the geometrically isomeric dimethyl and diethyl esters of 3-methylcyclohexene-4-dicarboxylic acid (from piperylene) with 2.5 or with 5 moles CH_3MgI gave a mixture of the corresponding diketones and glycols.

A liquid substance was again isolated when working with the cis-isomer. This liquid deposited a small amount of crystals on standing. On the basis of analytical data the latter substance was assigned formula (XI).



(XI)

Mixtures of diketones and glycols were subjected to dehydration by heating with acetic anhydride at 230-240° for 12 hours. The glycols gave mixtures of unsaturated and aromatic hydrocarbons, while the diketones were recovered unchanged. Both diketones were crystalline substances with similar melting points.

Heating of a mixture of cis-diketone and glycol at 180-200° for 6 hours led to formation not of hydrocarbons but of the corresponding hexahydrobenzofuran, while the diketone was, as before, recovered unchanged.

Treatment of cis- and trans-forms of the dimethyl and diethyl esters of 4-methylcyclohexene-4-dicarboxylic acid (from isoprene) with 5 moles CH_3MgI gave crystalline cis- and trans-glycols. Heating of both glycols with acetic anhydride again yielded mixtures of unsaturated and aromatic hydrocarbons. When distilled (at the ordinary pressure) the cis-glycol gave the corresponding hexahydrobenzofuran. Treatment of the same isomeric esters with 2.5 moles CH_3MgI led only to a liquid substance which was identified as an unsaturated ketone.

Reaction of the isomeric esters of 3,6-dimethylcyclohexene-4-dicarboxylic acid (from dipropenyl) with 5 moles CH_3MgI gave only unsaturated ketones.

EXPERIMENTAL

I. Preparation of Esters of Cyclohexene-4-Dicarboxylic Acids

The substances named above were prepared by the previously described method [4]. For the present work, apart from the compounds already characterized, another three diethyl esters were prepared from: trans-6-methylcyclohexene-4-dicarboxylic acid (from piperylene and diethyl fumarate), trans-4-methylcyclohexene-4-dicarboxylic acid (from isoprene) and trans-3,6-dimethyl-cyclohexene-4-dicarboxylic acid (from dipropenyl). The constants of all the esters used in this work are set forth in Table 1. The analytical data for the esters prepared for the first time are given in Table 2.

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*Crystalline derivatives of unsaturated ketones with hydrazine derivatives (semicarbazide, 4-nitro- and 2,4-dinitrophenylhydrazines) could not be prepared.

TABLE 1

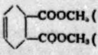
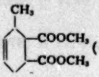
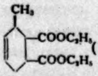
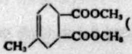
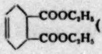
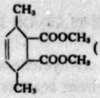
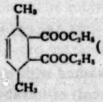
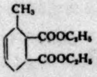
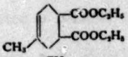
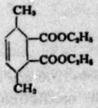
Substance	Boiling point	Pressure (in mm)	d_4^{20}	n_D^{20}	MR found	MR calculated
 (cis)	141.5—142°	20	1.1448	1.4729	48.56	49.02
(trans)	139 —139.5	20	1.1269	1.4680	48.93	49.02
 (cis)	144 —145	20	1.1101	1.4706	53.40	53.64
 (trans)	152 —153	20	1.0409	1.4604	63.25	62.87
 (cis)	149 —150	20	1.1139	1.4735	53.49	53.64
 (trans)	160 —161	20	1.0480	1.4620	63.05	62.87
 (cis)	154.5—155.5	20	1.0989	1.4736	57.80	58.26
 (trans)	148.5—149.5	10	1.0389	1.4650	67.70	67.49

TABLE 2

Substance	Found (%) C	Found (%) H	Found (%) OC_2H_5	Calculated (%) C	Calculated (%) H	Calculated (%) OC_2H_5
 (trans)	65.13	8.38	36.51	64.97	8.39	36.65
 (trans)	65.14	8.56	36.69	64.97	8.39	36.65
 (trans)	66.55	8.75	34.84	66.12	8.72	35.14

II. Preparation of Hydroaromatic Diketones and Glycols

The reaction of dimethyl and diethyl esters of cis- and trans-Δ^4-tetrahydrophthalic acid and its homologs with methyl magnesium iodide was performed under the usual conditions. 0.1 mole of diester was added, with cooling and stirring, to a solution of organomagnesium compound prepared from 0.25 or 0.5 g-atom magnesium and 0.3-0.6 mole methyl iodide in 200 ml absolute ether. The mixture was then heated for 2 hours on a water bath and left overnight. The organomagnesium complex was decomposed in the usual manner. The ethereal solution was dried over sodium sulfate and the ether was driven off on a water bath.

1) 3.5 g diketone and 5.3 g unsaturated ketone (cis-1-acetyl-2-isopropenyl-cyclohexene-4) were obtained from 6 g magnesium, 35.5 g methyl iodide and 31.5 g dimethyl ester of cis-cyclohexene-4-dicarboxylic acid (from butadiene and dimethyl maleate).

The diketone was recrystallized from aqueous methanol. M.p. 70°.

Found %: C 72.55; H 8.33. $C_{10}H_{14}O_2$. Calculated %: C 72.25; H 8.49.

The ketone boils at 93-95° (20 mm).

d_4^{20} 0.9660, n_D^{20} 1.4908, MR 49.22; calc. 49.87.
Found %: C 80.09; H 9.55. $C_{11}H_{16}O$. Calculated %: C 80.44; H 9.82.

From 2.5 g magnesium and 15 g methyl iodide and 3.5 g diketone was obtained 2.1 g (51% on the diketone) glycol.

M.p. 119.5-120.5° (from aqueous methanol).

Found %: C 72.97; H 11.16; OH 16.80. $C_{12}H_{22}O_2$. Calculated %: C 72.68; H 11.18; OH 17.15.

From 18 g magnesium, 106.5 g methyl iodide and 29.7 g dimethyl ester of cis-cyclohexene-4-dicarboxylic acid was obtained 23 g (76.9% on the diester) of glycol. M.p. 119.5-120.5° (from aqueous methanol).

Found %: C 72.86; H 10.87; OH 17.46. $C_{12}H_{22}O_2$. Calculated %: C 72.68; H 11.18; OH 17.15.

3 g glycol was distilled with 10% oxalic acid solution. The substance was washed with sodium carbonate solution and then with water and dried over sodium sulfate. 1.8 g (28% on the glycol) of hexahydrobenzofuran is obtained.

B.p. 97.5-98.5° (20 mm), d_4^{20} 0.9441, n_D^{20} 1.4778, MR 54.04; calc. 54.39.
Found %: C 79.71, 79.79; H 11.30, 11.41. $C_{12}H_{20}O$. Calculated %: C 79.94; H 11.18.

2) From 6 g magnesium, 35.5 g methyl iodide and 23.5 g dimethyl ester of trans-cyclohexene-4-dicarboxylic acid (from butadiene and dimethyl fumarate) were obtained 5.4 g diketone and 7 g unsaturated ketone (trans-1-acetyl-2-isopropenylcyclohexene-4).

The diketone melted at 114° (from aqueous methyl alcohol).

Found %: C 72.54; H 8.54. $C_{10}H_{14}O_2$. Calculated %: C 72.25; H 8.49.

The unsaturated ketone boiled at 91-92° (20 mm).

d_4^{20} 0.9630, n_D^{20} 1.4872, MR 49.07; calc. 49.87.
Found %: C 80.18; H 9.71. $C_{11}H_{16}O$. Calculated %: C 80.44; H 9.82.

The infrared spectrum of the unsaturated ketone was plotted in the 1600-1900 cm^{-1} region. Two absorption bands were found at 1645 and 1720 cm^{-1}. The first was attributed to the oscillations of the C=C bonds and the second to the C=O bond. The spectra were plotted with the IKS-6 spectrophotometer using a NaCl prism. The thickness of the layer of substance was 21 μ.

2 g unsaturated ketone was heated for 1 hour on a water bath with 2.7 g acetic acid and 1.2 ml concentrated hydrochloric acid. The mixture was then diluted with water and the substance distilled off with steam. The unsaturated ketone, after washing with NaOH solution and drying with sodium sulfate, was distilled in vacuum: b.p. 97-98.5° (20 mm), d_4^{20} 0.9439, n_D^{20} 1.4772, in agreement with the constants of the original substance.

From 4 g magnesium, 24 g methyl iodide and 5.4 g diketone was obtained 3.6 g (55.8% on the diketone) of glycol.

The glycol melts at 105-106° (from aqueous methanol).

Found %: C 72.52; H 11.23; OH 16.73. $C_{12}H_{22}O_2$. Calculated %: C 72.68; H 11.18; OH 17.15.

From 19 g magnesium, 110 g methyl iodide and 31.5 g dimethyl ester of trans-cyclohexene-4-dicarboxylic acid was obtained 21 g (66% on the ester) of glycol. M.p. 105-106°.

Found %: C 72.76; H 11.46; OH 17.02. $C_{12}H_{22}O_2$. Calculated %: C 72.68; H 11.18; OH 17.15.

3) From 7.2 g magnesium, 42.6 g methyl iodide and 21.2 g dimethyl ester of cis-6-methylcyclohexene-4-dicarboxylic acid (from piperylene and dimethyl maleate) was obtained 8.6 g of a mixture of diketone and glycol and 4.8 g of unsaturated ketone (cis-1-acetyl-2-isopropenyl-6-methylcyclohexene-4), from which a small quantity of stout crystals of the ketoester with m.p. 53-54.5° came down after prolonged standing.

Found %: C 67.52, 67.64; H 8.34, 8.56. $C_{11}H_{16}O_3$. Calculated %: C 67.32; H 8.21.

The unsaturated ketone boils at 100-102° (20 mm).

d_4^{20} 0.9349, n_D^{20} 1.4838, MR 54.51; calc. 54.49.
Found %: C 80.62; H 10.02. $C_{12}H_{18}O$. Calculated %: C 80.85; H 10.18.

12 g of the mixture of diketone and glycol and 12 g acetic anhydride were heated in a sealed glass tube at 180-200° for 6 hours. The mixture was distilled with steam. The liquid product was washed with sodium carbonate solution and with water, and dried over sodium sulfate. 2.3 g diketone and 4.1 g of the corresponding hexahydrobenzofuran were obtained.

The diketone melted at 101-102°.

Found %: C 72.94; H 8.88. $C_{11}H_{16}O_2$. Calculated %: C 73.30; H 8.94.

Hexahydrobenzofuran boiled at 103.5-104.5° (20 mm).

d_4^{20} 0.9302, n_D^{20} 1.4745, MR 58.76; calc. 59.01.
Found %: C 80.26, 80.51; H 11.38, 11.66. $C_{13}H_{22}O$. Calculated %: C 80.35; H 11.42.

From 18 g magnesium, 107 g methyl iodide and 32 g dimethyl ester of cis-6-methylcyclohexene-4-dicarboxylic acid was obtained 16 g of a mixture of diketone and glycol.

7.3 g of the mixture of diketone and glycol and 15 g acetic anhydride were heated at 230-240° for 12 hours. 2.7 g diketone and 2.1 g of hydrocarbons were obtained.

The diketone melted at 101-102°.

Found %: C 73.23; H 8.82. $C_{11}H_{16}O_2$. Calculated %: C 73.30; H 8.94.

4) From 15 g magnesium, 89 g methyl iodide and 26.2 g diethyl ester of trans-6-methylcyclohexene-4-dicarboxylic acid (from piperylene and diethyl fumarate) was obtained 13.4 g of a mixture of diketone and glycol. This amount of mixture and 25 g acetic anhydride were heated at 230-240° for 12 hours. Distillation of the mixture with steam gave 4.5 g diketone and 4.4 g hydrocarbons.

The diketone melted at 97.5-98.5° (from aqueous methanol).

Found %: C 73.66; H 9.23. $C_{11}H_{16}O_2$. Calculated %: C 73.30; H 8.94.

From 7.2 g magnesium, 42.6 g methyl iodide and 24 g diethyl ester was obtained 10.7 g of the mixture of diketone and glycol. The glycol was converted into hydrocarbon by the above method, and the diketone was recovered.

The diketone melted at 98-98.5°.

Found %: C 73.42; H 9.07. $C_{11}H_{16}O_2$. Calculated %: C 73.30; H 8.94.

5) From 18 g magnesium, 107 g methyl iodide and 32.2 g dimethyl ester of cis-4-methylcyclohexene-4-dicarboxylic acid (from isoprene and dimethyl maleate) was obtained 19.9 g (61.8% on the ester) of glycol.

The glycol melted at 81.5-82.5° (from aqueous methanol).

Found %: C 73.18; H 11.27; OH 16.04. $C_{13}H_{22}O_2$. Calculated %: C 73.53; H 11.39; OH 16.01.

7 g of the glycol and 6 g acetic anhydride were heated at 180-200° for 6 hours to give 4.3 g (67% on the glycol) of the corresponding hexahydrobenzofuran.

B.p. 103-105° (20 mm), d_4^{20} 0.9268, n_D^{20} 1.4778, MR 59.32; calc. 59.01.
Found %: C 80.54; H 11.26. $C_{13}H_{22}O_2$. Calculated %: C 80.35; H 11.42.

From 2 g magnesium, 12 g methyl iodide and 7 g dimethyl ester was obtained 2.7 g (42% on the ester) of unsaturated ketone (cis-1-acetyl-2-isopropenyl-4-methylcyclohexene-4).

B.p. 110-112° (20 mm), d_4^{20} 0.9355, n_D^{20} 1.4830, MR 54.42; calc. 54.49.
Found %: C 80.53, 80.85; H 9.99, 10.28. $C_{12}H_{18}O$. Calculated %: C 80.85; H 10.18.

6) From 14 g magnesium, 85 g methyl iodide and 25 g diethyl ester of trans-4-methylcyclohexene-4-dicarboxylic acid (from isoprene and diethyl fumarate) was obtained 21 g (95.4% on the ester) of glycol with m.p. 95-96° (from aqueous methanol).

Found %: C 73.82; H 11.68; OH 15.90. $C_{12}H_{22}O_2$. Calculated %: C 73.53; H 11.39; OH 16.01.

From 2 g magnesium, 12 g methyl iodide and 8 g diethyl ester was obtained 3.1 g (52.5% on the ester) of unsaturated ketone (trans-1-acetyl-2-isopropenyl-4-methylcyclohexene-4).

B.p. 106-108° (20 mm), d_4^{20} 0.9432, n_D^{20} 1.4851, MR 54.40; calc. 54.49.
Found %: C 80.62, 80.65; H 10.40, 10.46. $C_{12}H_{18}O$. Calculated %: C 80.85; H 10.18.

7) From 12 g magnesium, 71 g methyl iodide and 22.6 g dimethyl ester of cis-3,6-dimethylcyclohexene-4-dicarboxylic acid (from dipropenyl and dimethyl fumarate) was obtained 7.2 g (37.5% on the ester) of unsaturated ketone (cis-1-acetyl-2-isopropenyl-3,6-dimethylcyclohexene-4).

B.p. 109-110° (20 mm), d_4^{20} 0.9297, n_D^{20} 1.4830, MR 59.08; calc. 59.11.
Found %: C 81.22, 81.21; H 10.34, 10.52. $C_{13}H_{20}O$. Calculated %: C 81.19; H 10.48.

8) From 12 g magnesium, 71 g methyl iodide and 23.4 g diethyl ester of trans-3,6-dimethylcyclohexene-4-dicarboxylic acid (from dipropenyl and diethyl fumarate) was obtained 6.7 g (37.8% on the ester) of unsaturated ketone (trans-1-acetyl-2-isopropenyl-3,6-dimethylcyclohexene-4).

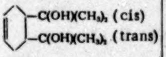
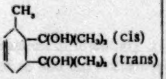
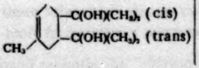
B.p. 103.5-104° (20 mm), d_4^{20} 0.9376, n_D^{20} 1.4905, MR 59.35; calc. 59.11.
Found %: C 81.32, 81.29; H 10.74, 10.32. $C_{13}H_{12}O$. Calculated %: C 81.19; H 10.48.

III. Preparation of the Hydrocarbons

Dehydration of the glycols was effected by heating with a one-half excess of acetic anhydride in sealed glass tubes at 230-240° for 12 hours. The products of dehydration were distilled with steam and then washed with sodium carbonate solution and with water. They were dried over sodium sulfate. Dehydration of the glycols gave the corresponding aromatic hydrocarbons with an admixture of unsaturateds.

The constants of the products of dehydration and the analytical data are presented in Table 3.

TABLE 3

Starting glycol	Constants of products of dehydration			MR		found (%)		calculated (%)	
	Boiling point at 20 mm	d_4^{20}	n_D^{20}	found	calcu-lated	C	H	C	H
 $-C(OH)(CH_3)_2$ (cis)	91—92.5°	0.8733	1.4960	54.27	54.01	88.93	10.87	88.82	11.18
$-C(OH)(CH_3)_2$ (trans)	91—92	0.8824	1.5028	54.34	54.01	89.14	10.85	88.82	11.18
 $-C(OH)(CH_3)_2$ (cis)	105—107	0.9023	1.5084	58.33	58.63	88.90	11.23	88.57	11.43
$-C(OH)(CH_3)_2$ (trans)	104.5—106	0.8821	1.5031	59.03	58.63	88.83	11.30	88.57	11.43
 $-C(OH)(CH_3)_2$ (cis)	106—106.5	0.8781	1.4968	58.37	58.63	88.64	11.77	88.57	11.43
$-C(OH)(CH_3)_2$ (trans)	105.5—106	0.8743	1.4985	59.15	58.63	88.38	11.37	88.57	11.43

0.2602 g of product of dehydration of a glycol (from dimethyl ester of cis-4-methylcyclohexene-4-dicarboxylic acid) was treated with a solution of 0.4707 g bromine in 10 ml chloroform; after standing for 24 hours, substitution had taken place of 0.3756 g bromine and addition of 0.03756 g.

To 0.4474 g of product of dehydration of a glycol (from the dimethyl ester of trans-cyclohexene-4-dicarboxylic acid) was added 0.520 g bromine in 10 ml chloroform. After standing for 36 hours, 0.192 g had undergone substitution and 0.148 g had undergone addition.

In the first case, therefore, the content of unsaturated hydrocarbons is 5.3%; in the second case it is 8.8%.

SUMMARY

1. The reaction of CH_3MgI with the dimethyl and diethyl esters of cyclohexene-4-dicarboxylic acid and its homologs was investigated.

2. A series of hydroaromatic glycols, diketones and unsaturated ketones are described.

3. Dehydration of the cis-forms of the unsaturated glycols prepared may, depending upon the conditions, go either with formation of the corresponding hexahydrobenzofurans or with formation of aromatic hydrocarbons.

4. The trans-forms of the same glycols yield only aromatic hydrocarbons on dehydration.

5. Only unsaturated ketones are formed by the action of CH_3MgI on the dimethyl and diethyl esters of 3,6-dimethylcyclohexene-4-dicarboxylic acid.

LITERATURE CITED

[1] A. A. Petrov and N. P. Sopov, J. Gen. Chem. 22, 591 (1952) (T.p. 653).*

[2] A. A. Petrov and N. P. Sopov, J. Gen. Chem. 22, 890 (1952) (T.p. 949).*

[3] A. A. Petrov and N. P. Sopov, J. Gen. Chem. 25, 517 (1955) (T.p. 485).*

[4] A. A. Petrov and N. P. Sopov, J. Gen. Chem. Supp. Vol. II, 853 (1953).

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*T.p. = C. B. Translation pagination.

TRANSFORMATIONS OF PINACONES CONTAINING SUBSTITUTED ACETYLENIC RESIDUES

XI. ACTION OF MERCURIC CHLORIDE AND BROMIDE ON UNSYMM. DIMETHYL-PHENYL-PHENYLETHINYL-ETHYLENE GLYCOL

E. D. Venus-Danilova and A. Fabritsy

Transformations of ditertiary α-glycols of the acetylenic series in presence of sulfuric acid have been studied by one of us and her collaborators with reference to a large number of substances [1]; it was then established that these substances, depending upon the structure, form substituted hydroxydihydrofurans or acetylenic ketones or, most frequently, a mixture of ketones and hydroxydihydrofurans.

We found recently that unsymm. dimethyl-phenyl-tert.-butylethinyl-ethylene glycol reacts with mercuric chloride to form a complex salt of 5,5-dimethyl-2-tert.butyl-4-phenyl-2-hydroxydihydrofuran-2,5. The same salt was also obtained from 5,5-dimethyl-2-tert.-butyl-4-phenyl-2-hydroxydihydrofuran-2,5 by the action on it of mercuric chloride in presence of a few drops of hydrochloric acid in alcohol [2].

It was therefore of interest to make a closer study of the transformation of ditertiary acetylenic α-glycols under the influence of salts of mercury, since secondary-tertiary acetylenic glycols [3] and a primary-tertiary [4] acetylenic α-glycol form substituted furans in alcoholic solutions of mercuric chloride.

It is known from the extensive literature that salts of mercury (chloride, sulfate and acetate), in reactions with acetylenic and enynic alcohols, as well as with α- and γ-glycols of the acetylenic series, can bring about isomerization [5], hydration [6] or dehyration with isomerization of these compounds [3, 4].

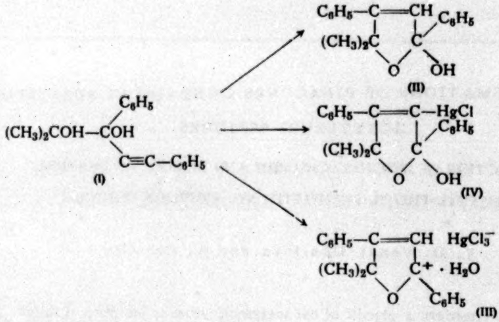
In the first place we investigated the transformation of unsymm. dimethyl-phenyl-phenylethinyl-ethylene glycol (2-methyl-3,5-diphenylpentyn-4-diol-2,3) (I) in presence of mercuric chloride and mercuric bromide.

In the action on the glycol of mercuric chloride in alcoholic solution with heating, two results were possible: a) Three substances were obtained: 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 (II), its mercury complex (III), and the organomercury compound (previously described by us) 5,5-dimethyl-2,4-diphenyl-3-chloromercuri-2-hydroxydihydrofuran-2,5; b) 2-methyl-3,5-diphenyl-4-chloromercuripenten-3-ol-2-one-5 (IVa) was formed, i.e. the open form of compound (IV) (Scheme 1).

The organomercury compound, formed as our experiments showed by the action of mercuric chloride on the acetylenic glycol (I), was not isolated in the pure from but in the form of the product of its symmetrization $C_{36}H_{32}O_3Hg$ (V) [internal ether of di-(5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuryl-2,5')-mercury]. The latter was obtained by the action of gaseous ammonia [8] on the mixture of hydroxydihydrofuran and the organomercury compound.

Two reactions probably take place when mercuric chloride acts on the acetylenic glycol (I): transformation of the glycol into the hydroxydihydrofuran and formation of the organomercury compound with liberation of hydrogen chloride which, together with the hydroxydihydrofuran and mercuric chloride, enters into the mercury complex (III); consequently, the reaction of the glycol with mercuric chloride gives equivalent amounts of the organomercury compound (IV) and the mercury complex (III), while part of the hydroxydihydrofuran and the equivalent amount of mercuric chloride remain in the mixture of products of reaction. The whole of the hydroxydihydrofuran can be converted into the mercury complex by addition of a sufficient amount of hydrochloric acid. In this manner the reaction of the glycol with formation of organomercury compound can be avoided.

Scheme 1



It must be assumed that the isomerization of glycol (I) to the hydroxydihydrofuran (II) proceeds more rapidly than the reaction of glycol with mercuric chloride, since free hydroxydihydrofuran remains in the mixture of reaction products. The hydroxydihydrofuran itself is not mercurated by mercuric chloride, as was proved in a special experiment.

The problem of the formation of the 2-hydroxydihydrofuran-2,5 from the glycol (I) in presence of mercuric chloride remains open. It has not been established whether the glycol directly isomerizes to the hydroxydihydrofuran or whether the glycol is first hydrated at the triple bond with formation of the β-ketoglycol $(CH_3)2COH\text{-}COH(C_6H_5)CH_2COC_6H_5$, subsequently dehydrated to the ethylenic γ-ketoalcohol and which finally cyclizes to the 2-hydroxydihydrofuran-2,5 (II). In none of the experiments with mercuric chloride did we succeed in isolating or detecting the β-ketoglycol. This substance must be unstable due to the great mobility of the hydrogen atoms of the methylene group situated between the carbonyl and alcoholic groups, thereby facilitating dehydration [9-11].

Isomerization of the glycol was found to take place in presence of 20% hydrochloric acid, but the yield of 2-hydroxydihydrofuran-2,5 did not exceed 52% due to fairly severe resinification.

It may be suggested that reaction of the acetylenic glycol with mercuric chloride with formation of the organomercury compound (IV or IVa) proceeds according to Scheme 2.

Cyclization of the organomercury compound (IVa), corresponding to the olefinic γ-ketoalcohol, possibly takes place in the instant of action of ammonia, and the open form (IVa) is also not excluded for the organomercury compound formed from the glycol in addition to the cyclic form (IV).

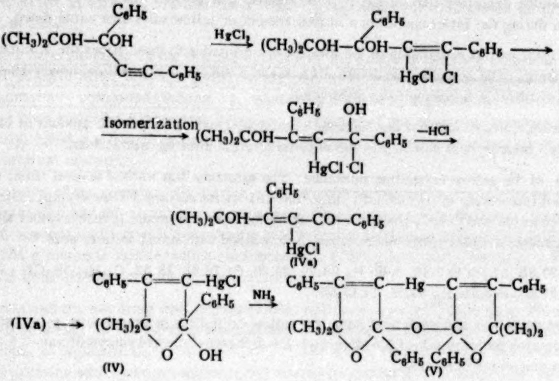
Mercuric bromide likewise acts on the glycol to form a mercury complex $C_{18}H_{17}OHgBr_3 \cdot H_2O$. This has been described before [7]. We did not isolate or investigate the organomercury compound and hydroxydihydrofuran in this experiment.

EXPERIMENTAL

I. Action of Mercuric Chloride on Unsymm. Dimethyl-phenyl-phenylethinyl-ethylene Glycol

A series of experiments was performed whose results are detailed in the table. The procedure was the same in all cases. One mole each of glycol and mercuric chloride were reacted, except in experiments 1 and 2 (0.25 mole mercuric chloride) and experiment 6 (2 moles mercuric chloride). The amount of ethyl alcohol (96%) was ten times that of the glycol. The mixture of glycol, mercuric chloride and alcohol was heated with stirring in a flask with a reflux condenser while vigorously boiling for 1 to 6 hours.

Scheme 2



TABLE

Experiment number	Amount of glycol (g)	Amount of $HgCl_2$ (g)	Duration of heating (hours)	Amount of complex obtained (g)	Yield of complex in relation to glycol taken (%)	Yield of complex (%)	Time between pouring off and separation of precipitate (min.)	Amount of hydroxydihydrofuran	Results
1	10	2.5	6	0.90	9	4.2	–	8	In sealed tube with anhydrous alcohol at 95°
2	10	2.5	4	2.30	23	10.6	60	8	All subsequent experiments were carried out in boiling 96% alcohol in quantity equal to ten times the quantity of glycol
3	5	5	6	3.23	65	30.6	10	–	
4	5	5	1	4.70	94	43.5	10	–	
5	2	2	1	1.65	83	38.3	10	–	
6	3	6	1	3.60	120	55.0	1	2	With equimolar amounts of glycol and mercuric chloride. The yield of complex is given after recrystallization from methanol
7	3	3	1	5.90	197	93.0	3	Traces	1.5 ml conc. HCl added to the mercuric chloride

In the first experiment anhydrous alcohol was used and heating was effected at 95° in a sealed tube for 6 hours. Glycol and mercuric chloride usually went into solution after gentle heating; the solution then turned yellow and very quickly deposited fine, bright-yellow crystals. The product was filtered and the alcohol distilled off in low vacuum; during the latter operation a further amount of yellow substance came down.

The residue after partial distillation of the alcohol was diluted with three times the volume of water and extracted with benzene. The benzene was driven off to leave a viscous, light-yellow, honey-like substance which decomposed when distillation in vacuum was attempted.

Ether extraction, carried out after the benzene extraction, gave a very minute amount of black sticky mass containing mercury. Mercury was detected in the aqueous solution after the extractions.

Examination of the yellow crystalline substance. The substance was washed several times with small portions of cold alcohol (preferably ethyl alcohol). M.p. 160-161° (with decomp.) after drying. The substance contains mercury and chlorine and gives a positive reaction for the hydroxyl group; it reacts rather slowly with potassium permanganate; a violet-green fluorescence is developed with strong sulfuric acid.

Found %: C 37.83, 37.68; H 3.42, 3.49; H_g 34.70, 35.20; Cl 18.68, 18.52. $C_{18}H_{17}OH_gCl_3 \cdot H_2O$. Calculated %: C 37.63; H 3.31; H_g 34.96; Cl 18.55.

Judging by its properties and analytical data, the yellow crystalline substance with m.p. 160-161° (with decomp.) is the complex mercury salt of 3,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 [7] which we described in the preceding communication.

Hydrolysis of the mercury complex with water goes very slowly. After 4 hours heating of 0.5 g mercury complex with 100 ml water on a boiling water bath, the amount of complex decreases, but after cooling the greater part of it again comes down. 0.3 g anhydrous sodium carbonate was added to the light-green, hot solution after a further 2-hours heating to bind the hydrochloric acid which had been released and to precipitate the mercury ion. A yellowish-brown mercury-containing precipitate at once came down and the solution lost its color. The precipitate of basic mercury salts and hydrous mercuric oxide was washed several times with hot benzene and the solution was extracted with benzene. Crystals of 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 came down after removal of the benzene; the crystals melted at 100-101° after purification and did not give a depression with authentic hydroxydihydrofuran. A characteristic violet-green fluorescence appeared on treatment with concentrated sulfuric acid.

Hydrolysis goes with very much greater facility if sodium carbonate solution is added at the start. The mixture quickly darkens on heating 10 g mercury complex with 100 ml 3% sodium carbonate solution (the theoretical amount is 100 ml of 2.8% solution), and much brown precipitate comes down after 2 hours. After the usual separation of the hydrolysis product, 4.07 g hydroxydihydrofuran was obtained (the theoretical amount is 4.63 g).

Analysis of the honey-like substance obtained by the action of mercuric chloride on the glycol. The substance was obtained after separation of the mercury complex; it contains mercury, gives a positive reaction with methyl magnesium iodide, reacts fairly rapidly with potassium permanganate, and dissolves in strong sulfuric acid with a violet-green fluorescence. After standing for 1-2 months, the honey-like substance gradually begins to deposit colorless crystals and changes into a solid mass permeated with a viscous liquid. The whole was triturated with cold ligroine; the solid was filtered, washed with ligroine and hexane and recrystallized from ether-hexane (1:2). The stout, colorless crystals with m.p. 99-100° did not give a melting point depression with authentic 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 and exhibited all the reactions characteristic of this substance. From 6 g honey-like substance after recrystallization was obtained 2.22 g of the 2-hydroxydihydrofuran-2,5 (table, Experiment 2).

From the thick liquid, containing organomercury compound, remaining after separation of the 2-hydroxydihydrofuran-2,5, the product of symmetrization was obtained by passing gaseous ammonia into a chloroform solution of this liquid [8]. A precipitate of NH_2H_gCl [12] at once came down. The latter was filtered and the solution was left for evaporation of the chloroform. The colorless crystalline substance was easily washed free from oily impurity with alcohol and acetone. A finely crystalline, colorless powder was obtained with m.p. 203-204° (partial decomposition) (V), which may be called the internal ether of di-(5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuryl-2,5')-mercury.

The compound is very poorly soluble in alcohol, acetone and benzene, and very easily soluble in chloroform; it contains mercury; reactions for chlorine, hydroxyl and carbonyl were negative.

Found %: C 61.00; H 4.89; Hg 27.52. M 714.8, 720. $C_{36}H_{32}O_3Hg$ (V). Calculated %: C 60.62; H 4.49; Hg 28.15. M 712.6.

Quantitative determination, in the mixture obtained by the action of mercuric chloride on unsymm. dimethyl-phenyl-phenylethinyl-ethylene glycol, of the mercury complex of the 2-hydroxydihydrofuran-2,5 and of the organomercury compound (Scheme 1). Heating of 2 g glycol, 2 g mercuric chloride and 20 ml 96% ethanol for 1 hour yielded 4.7 g mercury complex. Formation of this amount of complex (% Hg 34.96) required, in theory, 0.804 g mercuric chloride or 0.522 g mercury; the amount of glycol consumed was 0.79 g or 39.5% of the original amount.

After separation of the complex, distillation of the alcohol and addition of about 50 ml water, the 2-hydroxydihydrofuran-2,5 and the organomercury compound were extracted with benzene. Acidification of the remaining 50 ml aqueous solution with hydrochloric acid followed by passage of hydrogen sulfide resulted in separation of 0.251 g mercuric sulfide, which corresponded to 0.297 g mercuric chloride or 0.219 g mercury; i.e. 15% mercuric chloride had not entered into reaction.

The benzene extract was dried with sodium sulfate, and its volume was made up to 100 ml by addition of pure anhydrous benzene. In two parallel analyses with 20 ml each of this solution, determinations were made of the amount of organomercury compound as mercuric sulfide (evaporation of the benzene, addition of alcohol and precipitation with hydrogen sulfide); this treatment yielded 0.1378 g mercuric sulfide (mean of the two determinations), equivalent to 0.1184 g mercury. Consequently, the formation of the whole of the organomercury compound present in 100 ml of the benzene solution required 0.803 g mercuric chloride or 0.594 g mercury. In this case again, the calculated amount consumed in formation of the organomercury compound was likewise 39.5% of the original glycol. After driving off the benzene from the remaining 60 ml of benzene solution, 1.186 g of the viscous, honey-like substance was obtained, from which 0.21 g of the 2-hydroxydihydrofuran-2,5 was isolated. This signifies that a total of 0.35 g 2-hydroxydihydrofuran-2,5• was formed and this consumed 17.5% of the original glycol.

Action of mercuric chloride on unsymm. dimethyl-phenyl-phenylethinyl-ethylene glycol in presence of hydrochloric acid (table, Experiment 7). 3 g glycol, 3 g mercuric chloride, 3 ml alcohol and 1.4 ml hydrochloric acid (d 1.18) were heated to the boiling point of alcohol. The solution at once turned yellow, and after 3 minutes yellow crystals started to come down. Heating was continued for 20 minutes; another 0.5 ml hydrochloric acid was added, and then heating was continued for a further 40 minutes. After cooling, the precipitate was filtered, washed with alcohol and dried. Yield 5.4 g mercury complex. After driving off the alcohol and diluting the residue with water, a further 0.5 g mercury complex came down. Total yield 5.9 g (93%). Only traces of oil were obtained from the benzene extract.

Action of hydrochloric acid on unsymm. dimethyl-phenyl-phenylethinyl-ethylene glycol. 5 g glycol was heated to the boil with 10 ml 20% hydrochloric acid for 4 hours with vigorous stirring. A turbid, yellowish-green solution was obtained and a considerable quantity of resin. From the ethereal extract, after neutralization of the acid solution, was obtained 0.26 g (52%) 2-hydroxydihydrofuran-2,5, which gave all the characteristic reactions. From the acid solution was obtained 0.22 g viscous, brown resin.

II. Action of mercuric bromide on unsymm. dimethyl-phenyl-phenylethinyl-ethylene glycol

1 g glycol, 2.71 g mercuric bromide (1 mole glycol to 2 moles $HgBr_2$) and 20 ml 96% ethyl alcohol (more alcohol was needed than in the experiments with mercuric chloride because the bromide is less soluble in alcohol) were heated with stirring. The solution began to turn yellow after 10 minutes and a yellow precipitate came down. During the melting point determination the substance decomposed at the same temperature (180-183°) as the mercury complex, $C_{18}H_{17}OHgBr_3 \cdot H_2O$, obtained by the action of mercuric bromide on 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 in presence of hydrobromic acid [7]. Yield before recrystallization 2.2 g (84%). Analysis of the unrecrystallized substance gave a slightly low content of

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• Low results were probably obtained in isolating the 2-hydroxydihydrofuran-2,5. Part of this could remain in the products of mercuration and a part lost during recrystallization.

bromine and a too-high content of mercury*. Satisfactory results were obtained after recrystallization from methyl alcohol and washing with benzene.

When the glycol was treated with mercuric bromide in 1:1 ratio but in presence of 0.5 ml 45% hydrobromic acid, 1 g glycol yielded 1.5 g (56.4%) mercury complex after recrystallization from methyl alcohol.

Found %: Hg 27.91; Br 33.72. $C_{18}H_{17}OHgBr_3 \cdot H_2O$. Calculated %: Hg 28.35; Br 33.92.

SUMMARY

1. Reactions of unsymm. dimethyl-phenyl-phenylethinyl-ethylene glycol (2-methyl-3,5-diphenylpentyn-4-diol-2,3) ($C_{18}H_{18}O_2$) with mercuric chloride and bromide were studied.

2. Treatment of the glycol with mercuric chloride (1:1 molar ratio) gave a mercury complex $C_{18}H_{17}O \cdot HgCl_3 \cdot H_2O$, corresponding to 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 (from 39.5% of the original glycol), an organomercury compound (not isolated in the pure state) corresponding to mercurated 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 (likewise 39.5% of the original glycol), and 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 (17.5% of the original glycol). About 15-16% of the mercuric chloride remains unused.

3. Treatment of the organomercury compound with ammonia gave a heterocyclic product of symmetrization of the mercurated 2-hydroxydihydrofuran – the internal ether of di-(5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuryl-2,5')-mercury.

LITERATURE CITED

[1] E. D. Venus-Danilova, L. A. Pavlova, V. I. Şerkova and E. P. Brichko, Trans. Leningrad Inst. Technol. 1955, 30, 38.

[2] E. D. Venus-Danilova, A. Fabritsy and A. N. Orlova, J. Gen. Chem. 26, 1160 (1956) (T.p. 1317)**.

[3] E. D. Venus-Danilova and V. M. Albitskaya, J. Gen. Chem. 22, 5, 816 1568 (1952) (T. p. 879, 1611)**.

[4] L. A. Pavlova, J. Gen. Chem. 25, 1521 (1955) (T.p. 1471)**.

[5] Dupont, Compt. rend. 152, 1486 (1911); 153, 275 (1911); Johnson, J. Chem. Soc. 1946, 1014; Yu. S. Zalkind and V. N. Baranov, J. Gen. Chem. 10, 1432 (1940); A. I. Elizarova and I. N. Nazarov, Bull. Acad. Sci. USSR 1940, 2, 223 ff.; Heilbron, Jones and Smith, J. Chem. Soc. 1946, 54.

[6] Scheibler and Fisher, Ber. 55, 2903 (1922); Loquin and Sung, Bull. soc. chim. (4) 35, 604 (1924); A. E. Favorsky and A. S. Onishchenko, J. Gen. Chem. 11, III (1941); V. I. Nikitin, J. Gen. Chem. 15, 401 (1945); Lozach, Bull soc. chim. 11, 514 (1945); E. D. Venus-Danilova, A. P. Ivanov and L. I. Martynov, J. Gen. Chem. 21, 1806 (1951) (T.p. 1997)**.

[7] E. D. Venus-Danilova and A. Fabritsy, J. Gen. Chem. 26, 884 (1956) (T.p. 1007)**.

[8] Jenkins, J. Chem. Soc. 1921, 119, 747.

[9] E. D. Venus-Danilova and S. N. Danilov, J. Gen. Chem 2, 645 (1932).

[10] E. D. Venus-Danilova and M. V. Gorelik, J. Gen. Chem. 23, 1139 (1953) (T.p. 1193)**.

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* Contamination with organomercury compound may have been responsible for the unsatisfactory results of analysis before recrystallization of the complex.

** T. p. = C. B. Translation pagination.

[11] E. D. Venus-Danilova, M. V. Gorelik and T. A. Nikolaeva, J. Gen. Chem. 23, 1493 (1953) (T.p. 1561)*.

[12] B. V. Nekrasov, Course of Inorganic Chemistry (1948) 699.

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* T. p. = C. B. Translation pagination.

UNSATURATED CYCLIC HYDROCARBONS AND THEIR DERIVATIVES

XX. TRANSFORMATION OF METHYLCYCLOHEXENES AND METHYLCYCLOHEXADIENES INTO DINITROTOLUENES UNDER THE ACTION OF NITRATING MIXTURE

N. A. Domnin and V. A. Cherkasova

In a series of studies on halogenation-dehalogenation reactions we established a very pronounced tendency of unsaturated hydrocarbons and their halo derivatives of the cyclohexane series to change into benzene or its derivatives [1-4]. On the basis of the accumulated experimental material we proposed a mechanism of these transformations [17].

In the present communication we describe the transformation of methyleyclohexenes and methylcyclohexadienes into dinitrotoluenes under the action of nitrating mixture. Data are lacking at present for an interpretation of the mechanism of these transformations, but we think that something similar to the mechanism of joint halogenation-dehalogenation reactions is involved. Final proof, however, must await further investigations.

Several investigators have made brief and sketchy investigations of the formation of aromatic nitro derivatives by reaction of nitrating mixture with saturated and unsaturated hydrocarbons of the cyclohexane series [5-13]. No definite and trustworthy data on this problem, however, have appeared before in the literature. In our investigations we were compelled to reject nitration as a method of proof of the formation and structure of the aromatic compounds obtained from methylcyclohexenes and methylcyclohexadienes, since we have shown convincingly that these compounds themselves give the corresponding dinitrotoluenes.

EXPERIMENTAL

The starting substance for the preparation of methylcyclohexene was 1-methylcyclohexanol-2, which was dehydrated by heating with sulfuric acid [16]. In all probability we obtained a mixture of the two possible isomers — 1-methylcyclohexene-1 and 1-methylcyclohexene-2. Methylcyclohexadiene-1, 3 was prepared by the action of bromine on the methylcyclohexenes followed by heating of the dibromo compound with powdered potassium hydroxide. The yield of hydrocarbon was about 30%. The hydrocarbon was washed, and dried (first with calcium chloride and then with metallic sodium), and then distilled over metallic sodium. The 105-112° fraction was collected. Judging by its boiling point, density and refractive index, the product was not a pure substance but a mixture of 1-methylcyclohexadiene-1,3 and 2-methylcyclohexadiene-1,3. The methylcyclohexene and methylcyclohexadiene-1,3 subjected to nitration were examined for their ultraviolet absorption spectra in order to confirm the absence of toluene.

The reaction (with nitrating mixture) was performed in a round-bottomed flask fitted with reflux condenser and a dropping funnel whose end was immersed in the nitrating mixture.

Reaction of methylcyclohexadiene-1,3 with nitrating mixture. 5 g methylcyclohexadiene-1,3 was added very cautiously and in small portions with constant shaking to a mixture of 3.5 ml nitric acid (d 1.42) and 4.1 ml sulfuric acid (d 1.84). Addition of each fresh portion of hydrocarbon was accompanied by a violent reaction with foaming and the appearance of a red color (rapid addition of hydrocarbon might even lead to flashing). After addition of the whole of the methylcyclohexadiene-1,3, the content of the flask was heated on a water bath at 70° until the violent foaming ceased. The flask was then cooled, and after 7 days a further 30 ml nitrating mixture was added at room temperature, addition of each portion being followed by heating at 70°. At this stage the liquid in the flask was orange-yellow and transparent, and an oily, porous crust floated on its surface. It was steam-distilled; after about 200 ml had come over, pale yellow needles began to collect in the condenser, and the distilled oil also crystallized (0.59 g). After two recrystallizations from alcohol, the crystalline product melted at 67.5-69°. A mixed melting test with authentic dinitrotoluene [14] melted at 68-69°. (Authentic dinitrotoluene – 1-methyl-2,4-dinitrobenzene – was prepared by nitrating 5 g toluene; like the investigated substance, it was recrystallized twice from alcohol; its m.p. was then 68°.)

A portion of the product obtained by nitration of methylcyclohexadiene-1,3 was coverted to the diamine by the method of Ipatieff and Schmerling [15]. Reduction went very vigorously with heat development. The diamine was treated with acetic anhydride. The diacetyl derivative was recrystallized from dilute alcohol and melted at 220-221°; a mixture with authentic diacetylaminotoluene (m.p. 224-226°) melted at 221-221.5°. The ultraviolet absorption spectrum of the product obtained by nitration of methylcyclohexadiene-1,3 was also plotted by the variable thickness method, using the ISP-22 spectrophotometer. The spectrum was identical with that of dinitrotoluene.

Reaction of methylcyclohexene with nitrating mixture. The reaction was conducted under the same conditions as with methylcyclohexadiene-1,3. 6 g methylcyclohexene (b.p. 106-109°) was added to a mixture of 3.5 ml nitric acid and 4.1 ml sulfuric acid. In all, 38.5 ml nitrating mixture was added in a week. The crystals (0.35 g) obtained after steam distillation were recrystallized from alcohol. A mixture with authentic 1-methyl-2,4-dinitrobenzene melted at 66.7-68°. A mixed melting test of the diacetyl derivative gave a melting point of 218-220.5°.

SUMMARY

1-Methyl-2,4-dinitrobenzene is formed by the action of nitrating mixture on methylcyclohexadiene-1,3 and methylcyclohexene under the conditions described.

LITERATURE CITED

[1] N. A. Domnin and V. A. Cherkasova, J. Gen. Chem. 17, 2283 (1947).

[2] N. A. Domnin, V. A. Cherkasova and S. N. Andreev, J. Gen. Chem. 21, 1818 (1951) (T.p. 2011)*.

[3] N. A. Domnin and V. A. Cherkasova, J. Gen. Chem. 22, 897 (1952) (T.p. 957)*.

[4] N. A. Domnin and V. A. Cherkasova, J. Gen. Chem. 23, 1731 (1953) (T.p. 1823)*.

[5] F. R. Vreden, J. Russ. Chem. Soc. 4, 256 (1872).

[6] O. Wallach, Ann. 258, 323 (1890).

[7] O. Wallach, Ber. 24, 1573 (1891).

[8] V. V. Markovnikov, Ann. 302, 7 (1898).

[9] C. Harries and B. Antoni, Ann. 328, 88 (1903).

[10] H. Maeyer, Ann. 433, 350 (1923).

[11] S. S. Nametkin, J. Gen. Chem. 6, 1166 (1936).

[12] Pictet, Anal. Chem. (9), 10, 299 (1918).

[13] Pictet, Compt. rend. 163, 358 (1916).

[14] Higginbottom, Reactions of Organic Compounds (Moscow, 1939), 62.

[15] W. Ipatieff and Schmerling, J. Am. Chem. Soc. 59, 1056 (1937).

[16] J. B. Senderens, Compt. rend. 154, 1168 (1912).

[17] N. A. Domnin, J. Gen. Chem. 16, 1729 (1946).

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* T. p. = C. B. Translation pagination.

UNSATURATED CYCLIC HYDROCARBONS AND THEIR DERIVATIVES

XXI. THE REACTION OF 1-METHYL-3,4-DIBROMOCYCLOHEXANE WITH QUINOLINE

N. A. Domnin and V. A. Cherkasova

Willstatter and Hatt [1] were the first to show that the reaction of 1,2-dibromocyclohexane with quinoline does not give a pure hydrocarbon but a mixture of cyclohexene, cyclohexadiene-1,3 and benzene. This interesting observation remained unexplained and no attempts were made to account for it. Only in 1946 did one of us put forward the hypothesis [2] that the formation of aromatic compounds in the reaction of halo derivatives of cyclohexane with quinoline is caused by joint halogenation and dehalogenation. In later years we undertook a number of investigations with halo derivatives of cyclohexane [3-6] which confirmed the validity of the earlier assumptions.

In connection with the study of joint halogenation-dehalogenation reactions, it was of interest to establish the course of the interaction of quinoline with halo derivatives of cyclohexane homologs. We have therefore studied the reaction of quinoline with 1-methyl-3,4-dibromocyclohexane. The resultant hydrocarbon mixture was washed with dilute sulfuric acid and with water, dried over calcium chloride and metallic sodium, and repeatedly fractionated.

It was established by ultraviolet absorption spectroscopy that the hydrocarbon mixture contains about 50% toluene. These results were obtained by reacting 1-methyl-3,4-dibromocyclohexane with quinoline in 3:2 ratio. The reaction was carried out many times and each time (without changing the ratio of components) we found toluene in the volatile fraction. Components of the hydrocarbon mixture obtained are probably methylcyclohexene and methylcyclohexadiene.

We have thus proved that, contrary to the statements of some investigators, it is inadvisable to apply the method of reaction of methyldibromocyclohexanes with quinoline for the preparation of methylcyclohexadienes-1,3.

In 1908 N. D. Zelinsky and A. I. Gorsky reacted 1-methyl-3,4-dibromocyclohexane with quinoline and obtained dihydrotoluene to which they assigned the structure of 1-methylcyclohexadiene-2,4 [7]. Since, however, this hydrocarbon did not show any increment of molecular refraction, the authors suggested that it might also possess a bicyclic structure.

On the basis of the observations in the present investigation, we can reasonably assume that the hydrocarbon obtained by N. D. Zelinsky and A. I. Gorsky was not an individual substance but a mixture of toluene, methylcyclohexene and methylcyclohexadiene.

EXPERIMENTAL

Reaction of 3,4-dibromo-1-methylcyclohexane with quinoline. The starting substance for the preparation of 3,4-dibromo-1-methylcyclohexane was methylcyclohexanol-4, which was converted by Senderens dehydration [8] into methylcyclohexene; a solution of bromine in chloroform was added dropwise to a cooled solution of methylcyclohexene in chloroform.

We first used 1-methylcyclohexanol-2. On dehydration of the latter, we probably obtained a mixture of two hydrocarbons (1-methylcyclohexene-1 and 1-methylcyclohexene-2), and treatment of this mixture with bromine probably gave a mixture of two dibromomethylcyclohexanes. We used the latter mixture in the reaction with quinoline without separating the components. In this case the toluene content of the hydrocarbon mixture was lower than in the product of interaction of 3,4-dibromo-1-methylcyclohexane with quinoline; we therefore describe here one of the reactions with the second dibromo product.

12 g freshly distilled 3,4-dibromomethylcyclohexane and 8 g quinoline, also freshly distilled, were carefully heated in a flask with side-tube until the first sign of reaction (a particularly wavy movement in the liquid, formation of golden, spherical droplets and a characteristic crackling). After the violent reaction had come to an end (layers had then formed in the flask), heating was continued. The distilled product (5.65 g) was washed with dilute sulfuric acid and then with water and dried with calcium chloride and metallic sodium. After repeated distillation and drying over sodium, the collected 104.5-108.5° fraction (3.6 g) did not contain bromine (Beilstein test) and had the following constants: $n_D^{16.5}$ 1.4688, $d_4^{16.5}$ 0.8393. The absorption spectrum of the alcoholic solution of this fraction, plotted in the SF-11 spectrophotometer, had the fine structure characteristic of toluene. The position of the maxima of the individual bands exactly coincided with the position of the corresponding maxima in the spectrum of authentic toluene. Apart from toluene, the fraction possibly contained two other compounds, most probably methylcyclohexene and methycyclohexadiene which have boiling points close to the boiling point of toluene. Although their absorption spectra overlapped with that of toluene, the fine structure was absent. Bearing in mind that the absorption spectra of all the compounds in the investigated fraction, except toluene, lack fine structure, and that consequently the change of absorption resulting from their presence is small within a narrow interval of wavelengths, we can easily calculate the precentage content of toluene in the reaction product obtained. The toluene content of the solution used for the spectrophotometric examination may be found from the formula:

$$C = \frac{D_1 - D_2}{d_1 - d_2} \cdot 100,$$

where C is the percentage content of toluene, D_1 and D_2 are the optical densities of a solution of known concentration of the investigated product at two slightly different wavelengths, d_1 and d_2 are the optical densities of toluene of the same concentration as the investigated product at the same wavelengths. Use was made for the calculation of the optical densities between points on the absorption curve at which the change of optical density was most abrupt, so that the error in determination of the toluene content was at a minimum (these were usually the maximum or minimum point and a point distant from it by 1.5-2 mμ).

The product of reaction of 3,4-dibromomethylcyclohexane with quinoline was found to contain approximately 53% toluene. Determination of the bromine number by the McIlhiney method [9] gave 57.7% toluene in the product. When determining the bromine number we took into consideration the fact that methylcyclohexadiene-2,4 readily adds on only the first molecule of bromine [7]. In this case the theoretical bromine number is 170, and that found by us for the reaction product is 72.

SUMMARY

Reaction of quinoline with 3,4-dibromo-1-methylcyclohexane gives toluene; the content of the latter in the reaction products reaches 53%.

LITERATURE CITED

[1] Willstätter and Hatt, Ber. 15, 1464 (1912).

[2] N. A. Domnin, J. Gen. Chem. 16, 1729 (1946).

[3] N. A. Domnin and V. A. Cherkasova, J. Gen. Chem. 17, 228 (1947).

[4] N. A. Domnin, V. A. Cherkasova and S. N. Andreev, J. Gen. Chem. 21, 1818 (1951) (T.p. 2011).*

[5] N. A. Domnin and V. A. Cherkasova, J. Gen. Chem. 22, 897 (1952) (T.p. 957).*

[6] N. A. Domnin and V. A. Cherkasova, J. Gen. Chem. 23, 1731 (1953) (T.p. 1823).*

---

* T. p. = C. B. Translation pagination.

[7] N. D. Zelinsky and A. I. Gorsky, J. Russ. Chem. Soc. 40, 1388 (1908).

[8] F. Senderens, Compt. rend. 154, 1168 (1912).

[9] Standard Methods for Testing Petroleum and its Products (1944), Ed. 5.

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THE CHLORINATION OF DICHLOROHEXADIENE AND THE DEHYDROCHLORINATION OF THE REACTION PRODUCTS

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1,3-Dichlorohexadiene-2,4 (I) is easily prepared by the hydrochlorination of divinylacetylene in presence of a catalyst (Cu_2Cl_2) [1, 2]:

$$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 \rightarrow \underset{(I)}{CH_2Cl{-}CH{=}CCl{-}CH{=}CH{-}CH_3}.$$

Dichlorohexadiene does not manifest a tendency to spontaneous polymerization, but it can serve as a starting substance for the synthesis of new polymerizable compounds. For this purpose, dichlorohexadiene is first converted by chlorination into polychlorides which by loss of hydrogen chloride change into the corresponding chlorohexatrienes. What at first sight appears to be a simple reaction between unsaturated hydrocarbons and chlorine, is actually an extremely complex process, because, in dependence upon the character of the starting olefins and the conditions of chlorination, the process may proceed by a heterolytic (electrophilic) or by a homolytic mechanism.

Unsaturated hydrocarbons with a normal chain usually add on chlorine at the double bond, but at high temperatures there are formed, apart from addition products, chloroolefins which are the result of "allylic" chlorination [3, 4]. Cleavage of hydrogen chloride was also observed [5] in the chlorination of 1,3-dichlorobutene-2. Reaction between halogens and olefins is regarded as a process of an acid-base character [6]. It has also been shown that chlorination of unsaturated hydrocarbons depends in great measure on the nature of the substituent attached to the methylene group [7, 8].

Chlorination of dichlorohexadiene (I) goes in two steps: the first molecule of chlorine adds on to dichlorohexadiene with formation of 1,2,3,5-tetrachlorohexene-3 (II), while a second molecule adds on with formation of 1,2,3,3,4,5-hexachlorohexane (III)

$$\underset{(II)}{CH_2Cl{-}CHCl{-}CCl{=}CH{-}CHCl{-}CH_3}, \qquad \underset{(III)}{CH_2Cl{-}CHCl{-}CCl_2{-}CHCl{-}CHCl{-}CH_3}$$

Since the first step goes very much more rapidly than the second step, hexachlorohexane only starts to form after nearly complete consumption of the original dichlorohexadiene. The over-all velocity of the process is appreciably increased in presence of traces of moisture. The structure of the tetrachlorohexene was established by ozonization. The structure of the hexachlorohexane may be represented by formula (III), since it can be formed from 1,2,3,5-tetrachlorohexene-3 (II) by addition of chlorine in the 3,4-position.

The presence of three atoms of saponifiable chlorine is revealed in tetrachlorohexene by the action of dilute alcoholic solutions of caustic alkali. Under similar conditions only four atoms of saponifiable chlorine are found in hexachlorohexane. In this reaction one molecule of HCl is evidently first split off with formation of

1,2,3,4,5-pentachlorohexene-3 (IV) which contains two atoms of chlorine at the double bond which are not susceptible to hydrolysis.

Under chlorination conditions dichlorohexadiene (I) not only adds on chlorine but also, to small extent, has a hydrogen substituted by chlorine, leading to formation of 1,3,6-trichlorohexadiene-2,4 (V); further chlorination of the latter gives 1,2,3,5,6-pentachlorohexene-3 (VI). The amount of hydrogen chloride released

$$CH_2Cl-CHCl-\underset{(IV)}{CCl}=CCl-CHCl-CH_3;\quad CH_2Cl-CH=\underset{(V)}{CCl}-CH=CH-CH_2Cl;$$

$$CH_2Cl-CHCl-\underset{(VI)}{CCl}=CH-CHCl-CH_2Cl$$

depends on the temperature of the reaction; it decreases appreciably with fall in temperature. Chlorination of dichlorohexadiene under otherwise identical conditions (1 mole chlorine per mole starting substance) gives 9.2 g HCl at 20° and 5.4 g at −40°. The resultant trichlorohexadiene (V) is further chlorinated with formation of the pentachlorohexene (VI) without any further evolution of hydrogen chloride.

The structure of the trichlorohexadiene was established by ozonization. The presence of two atoms of saponifiable chlorine in the molecule of trichlorohexadiene also shows the validity of the proposed structure, since other schemes of substitution of hydrogen by chlorine in dichlorohexadiene give trichlorohexadienes containing only 1 atom of saponifiable chlorine.

The pentachlorohexene (VI) undergoes chlorination and ozonization with much greater difficulty than tetrachlorohexene (II), possibly due to stereochemical factors. Treatment with dilute alcoholic alkali gives rather less than 4 atoms of saponifiable chlorine in pentachlorohexene (51.0% instead of the theoretical amount of 55.3%), which is evidently associated with the partial loss of HCl accompanying the formation of the double bond.

When the tetrachlorohexene (II) and the hexachlorohexane (III) are treated with concentrated solutions of caustic alkali, they easily split off hydrogen chloride with formation of, respectively, 2,3-dichlorohexatriene-1,3,5 (VII) and 2,3,4-trichlorohexatriene-1,3,5 (VIII). Although there are no direct proofs of the position of the chlorine atoms in the trienes synthesized, the following formulas are most probable on the basis of the structure of the starting substances:

$$CH_2=CCl-\underset{(VII)}{CCl}=CH-CH=CH_2,\quad CH_2=CCl-\underset{(VIII)}{CCl}=CCl-CH=CH_2.$$

These reactions proceed with great violence and are usually completed in 15-20 minutes. If, however, the solvent used is methyl alcohol, in which the reaction products and the starting substances possess limited solubility, the reaction mixture separates into layers before the reaction is completed, and the end of the reaction is thus delayed. In order to accelerate the process, the reaction mixture (after addition of the starting substance) was heated under a reflux condenser with intensive stirring for 20-30 minutes. Solid caustic alkalies may be replaced by their concentrated aqueous solutions, but in that case the rate of reaction is considerably retarded and the reaction is only completed after 5-6 hours. Unsatisfactory results followed attempts to conduct the reaction only with the help of concentrated sodium hydroxide solution (without methyl alcohol) with heating.

EXPERIMENTAL

Chlorination of dichlorohexadiene. A series of experiments was run with the objective of determining the dependence of the yields of reaction products on the temperature and degree of chlorination. Chlorination was performed in a reactor of the absorber type, fitted with a bubbler tube and thermometer, and gaseous chlorine was introduced into the dichlorohexadiene with external cooling. At the end of the experiment the dissolved hydrogen chloride was forced out by a stream of air, and the reaction mixture was fractionated in vacuum. 2 moles dichlorohexadiene (I) was taken in all experiments. The first chlorination step, i.e. formation of tetrachlorohexene (II), usually required about 1 ½ hours; the second stage took 7-8 hours. The amount of hydrogen chloride evolved during reaction was determined by absorption in alkali solution. Since the reaction between chlorine and dichlorohexadiene proceeds so violently that the whole of the added chlorine is almost completely absorbed, only the HCl is removed with inert gases. However, as the process comes towards its end, when approximately 1 mole chlorine has been absorbed per mole dichlorohexadiene, the gas stream also removes a small amount of chlorine, and its escape increases sharply after consumption of the dichlorohexadiene taken into reaction, i.e. when the primary reaction product (tetrachlorohexene) is chlorinated. Consequently, experiments in which the amount of liberated HCl was determined did not go to completion. Results obtained for determination of HCl in the exit gas after different intervals of time for one and the same experiment show that for a given rate of flow of chlorine the amount of HCl evolved remains constant (Table 1).

TABLE 1

Dependence of Yields of Reaction Products on the Temperature and Degree of Chlorination

Temperature	Increase in weight (in g)	Amount of HCl (g)	Amount of reaction products (g)						Yield of $C_6H_8Cl_4$ (in % of reacted $C_6H_8Cl_2$)
			$C_6H_8Cl_2$	$C_6H_7Cl_3$	$C_6H_8Cl_4$	$C_6H_7Cl_5$	$C_6H_8Cl_6$	Distillation residue	
20—25°	81.0	12.2	95.0	37.0	210.8	20.8	—	13.0	69.3
20—25	120.4	18.4	12.8	44.8	308.2	37.4	—	16.4	72.7
20—25	200.0		—	—	167.0	140.2	170.8	20.2	37.7
25—30	240.0		—	—	76.2	180.6	233.2	19.0	17.2
30—40	121.0	10.8	32.4	36.4	323.2	14.0	—	12.8	81.8

The data of Table 1 show that the yield of tetrachlorohexene, calculated on the reacted dichlorohexadiene, is at a given temperature substantially independent of the degree of chlorination within the limits of reaction of equimolar amounts of the starting substances. With further chlorination the yield of reaction product falls sharply because it is transformed into pentachlorohexene and hexachlorohexane. Lowering of the temperature leads to an increased yield of tetrachlorohexene because there is then less substitution of hydrogen in the methyl group by chlorine, leading to formation of trichlorohexadiene (V), than at higher temperatures.

In the chlorination of dichlorohexadiene a small amount of high-molecular substance is formed in addition to products of addition (tetrachlorohexene) and products of substitution of the hydrogen of the methyl group by chlorine; the yield of the high-molecular substance increases with progressive chlorination, but it remains nearly constant after reaction of equimolar amounts of components. Chlorination of tetrachlorohexene does not lead to such a residue, whose chlorine content does not differ from that of the original dichlorohexadiene. On the basis of these results we may infer that the distillation residue is the product of polymerization of dichlorohexadiene during its chlorination.

Ozonization of the reaction products. The substances under investigation were dissolved in chloroform (30-40 ml) and ozonized with oxygen containing 3-4% ozone with a velocity of 20-25 liters/hour, while the reactor was cooled to −50 to −60°. In all experiments, after removal of the chloroform, liquid transparent ozonides were found, whose decomposition by refluxing with water led in all cases to formation of two layers: a lower aldehydic layer and an upper aqueous-acidic layer. The upper layer was separated and examined for identification of the acids formed.

a) Ozonization of 12.5 g trichlorohexadiene (V) gave 18.7 g ozonide. The volatile portion of the acidic solution was distilled off at 100 mm. The total acidity was determined in the aqueous distillate (titration of a sample with 0.1 N KOH) and the content of hydrogen chloride was determined by the Volhard method. No appreciable amounts of volatile organic acids were found. Fractional distillation of 6.8 g of residue at 10 mm gave 3.8 g distillate with b.p. 83-84°, and 2.8 g of crystalline residue. Sublimation also occurred at the same

TABLE 2

Constants of Polychlorides and Chlorine Determinations

Formula of polychloride	Boiling point (10 mm)	d_4^{20}	n_D^{20}	MR_D		Total chlorine (%)		Hydrolyzable chlorine (%)	
				Found	Calculated	Found	Calculated	Found	Calculated
$CH_2Cl-CH=CCl-CH=CH-CH_2Cl$	80—83°	1.2873	1.5200	43.70	43.57	56.95. 57.53	57.40	38.12. 38.08	38.20
$CH_2Cl-CHCl-CCl=CH-CHCl-CH_3$	94—95	1.3656	1.5170	48.77	48.91	62.55. 63.76	63.50	47.00. 47.61	47.96
$CH_2Cl-CHCl-CCl=CH-CHCl-CH_2Cl$	108—111	1.4560	1.5170	54.10	53.38	69.13. 70.02	69.10	50.94. 51.69	55.30
$CH_2Cl-CHCl-CCl_2-CHCl-CHCl-CH_3$	125—126	1.5254	1.5320	59.15	59.11	71.44. 72.18	72.71	48.60. 49.23	48.50

time of a small amount of fine crystals which could be separated from the still uncrystallized distillate by decantation. The distillate crystallized on standing; m.p. 53.6°. The distillation residue and the decanted crystals had m.p. 98-99° after recrystallization from water.

The acid number found for the distillate was 593, 595. The calculated value for chloroacetic acid is 593. Acid number of residue: 872, 884. The calculated value for oxalic acid dihydrate is 889.

b) Ozonization of 15.8 g tetrachlorohexene (II) gave 18.9 g ozonide. Distillation of the aqueous residue in vacuum gave 10 g residue. Volatile acids were not detected in the distillate. The residue yielded 3 fractions (at 10 mm): 1st, 82-83°, 1.2 g; 2nd, 84-103°, 5.6 g; 3rd, 104-106°, 3.12 g. The third fraction crystallized; m.p. 48°.

Acid number of 1st fraction: 510, 500. Calculated for chloropropionic acid: 516.

Acid number of 3rd fraction: 398, 399. Calculated for dichloropropionic acid: 392.

c) Pentachlorohexene (VI) was ozonized with great difficulty. The chloroform solution had a deep blue color although the ozonization of the sample was far from completed. 13.4 g substance gave 15.6 g ozonide. Volatile acids were not detected in the aqueous distillate. The residue distilled at 104-105° (10 mm); m.p. 49°.

Acid number found: 392, 390. Calculated for dichloropropionic acid: 392.

The physical constants of the polychlorides synthesized and the results of analyses for total and saponifiable chlorine are presented in Table 2.

Dehydrochlorination of tetrachlorohexene. 0.4 ml methyl alcohol was placed in a reactor fitted with reflux condenser, stirrer, dropping funnel and thermometer. Addition was then made with cooling of 2.4 moles sodium hydroxide (part of the latter did not dissolve). To the solution, with vigorous stirring, was added 222 g tetrachlorohexene in the course of 15 minutes from the dropping funnel. The temperature was kept at 30-35° by cooling the reactor. The reaction mixture was then boiled for 30 minutes while stirring; thereupon it was poured into water (0.75 liter) and the separated (lower) oily layer was distilled in vacuum. Yield 128.0 g (82.5%) dichlorohexatriene (VII).

B.p. 65-68° (10 mm), d_4^{20} 1.1870, 1.5137, MR_D 37.8; Calculated: 38.24. Found %: Cl 48.11, 48.23. $C_6H_6Cl_2$. Calculated %: Cl 47.6.

Dehydrochlorination of hexachlorohexane. 1 mole hexachlorohexane (III) was run in the course of 20 minutes into an alcoholic solution of alkali (3.6 moles NaOH in

0.75 liter methanol). After boiling for 30 minutes, reaction mixture was run into water (1 liter), and the oily (lower) layer was distilled in vacuum to give 135 g (73.5%) trichlorohexatriene (VIII).

B. p. 75-78° (10 mm), d_4^{20} 1.3079, n_D^{25} 1.5288, MR_D 42.90; Calc. 43.11. Found %: Cl 57.65, 57.64. $C_6H_5Cl_3$. Calculated %: Cl 57.90.

The synthesized dichloro- and trichlorohexatrienes are liquids with characteristic odors. They slowly polymerize on standing with formation of white, ropy polymers, soluble in common solvents (except alcohols).

SUMMARY

1. Chlorination of 1,3-dichlorohexadiene-2,4 leads to formation of 1,2,3,5-tetrachlorohexene-3 and 1,2,3,3,4,5-hexachlorohexane. The main reaction product is tetrachlorohexene when using an equimolar ratio of components.

2. Chlorination of dichlorohexadiene is also accompanied by release of a small amount of hydrogen chloride with formation of 1,3,6-trichlorohexadiene-2,4, further chlorination of which gives 1,2,3,5,6-pentachlorohexene-3.

3. Treatment of tetrachlorohexene and hexachlorohexane with alcoholic solutions of caustic alkalies results in release of hydrogen chloride with formation of a dichlorohexatriene and a trichlorohexatriene respectively. The latter form polymers which dissolve in common organic solvents except alcohols.

LITERATURE CITED

[1] D. D. Coffman, J. A. Nieuwland and W. H. Carothers, J. Am. Chem. Soc. 55, 2051 (1933).

[2] A. E. Akopyan, J. Appl. Chem. 27, 639 (1954) (T.p. 601).*

[3] T. Stewart and B. Weidenbaum, J. Am. Chem. Soc. 58, 98 (1936)

[4] H. Croll and G. Hearn, Ind. Eng. Chem. 31, 1530 (1939).

[5] W. H. Carothers and C. I. Berchet, J. Am. Chem. Soc. 55, 1628 (1833).

[6] A. N. Titov and F. L. Maklyaev, J. Gen. Chem. 24, 1624 (1954). (T.p. 1607).*

[7] R. Kh. Freidlina, V. N. Kost and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 233 (T. p. 207).*

[8] A. N. Nesmeyanov, V. N. Kost and R. Kh. Friedlina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 258. (T. p. 209).*

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* T. p. = C. B. Translation pagination.

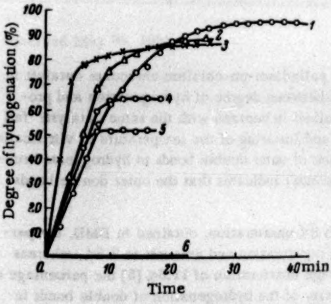
HYDROGENATION OF SOLUTIONS OF BUTADIENE RUBBER AT ATMOSPHERIC PRESSURE AND ROOM TEMPERATURE

II. INFLUENCE OF NATURE OF THE SOLVENT ON THE PROCESS OF CATALYTIC HYDROGENATION OF UNSATURATED COMPOUNDS OVER PALLADIUM - ON - CALCIUM CARBONATE CATALYST

A. I. Yakubchik and G. N. Gromova

An influence of the nature of the solvent on the process of catalytic hydrogenation of organic compounds has been observed by many investigators [1-4]. During hydrogenation in solution, the rate of hydrogenation and the percentage transformation (degree of hydrogenation) depend upon the relative adsorbability by the catalyst of the individual components of the system undergoing hydrogenation (unsaturated compound, products of catalytic reaction and solvent); the extent of adsorption is largely governed by the solvent.

With the objective of establishing the influence of the solvent on the rate and extent of hydrogenation of an unsaturated compound in presence of palladium-on-calcium carbonate catalyst, we carried out the hydrogenation of allyl alcohol with this catalyst in various solvents. Results are plotted in the diagram.



Influence of solvent on the degree of hydrogenation of allyl alcohol over palladium-on-calcium carbonate (catalyst 0.2 g, solvent 15 ml).
1) ethyl ether; 2) heptane; 3) ethyl alcohol;
4) 2,2-dimethyldioxane-1,5; 5) isoamyl alcohol;
6) benzene.

The diagram indicates that the solvent exerts a marked influence not only on the rate of hydrogenation of allyl alcohol over palladium-on-calcium carbonate catalyst (the slope of the initial portion of the curve), but also on the degree of hydrogenation. Thus, for example, in ethyl alcohol and pentane (2, 3) in presence of 0.2 g of the catalyst, allyl alcohol is hydrogenated to the extent of approximately 87%, in isoamyl alcohol (5) to the extent of 52%, in 2,2-dimethyldioxane-1,5 (4) to the extent of 65%, in diethyl ether (1) to the extent of 95%. Allyl alcohol does not undergo hydrogenation in benzene (6).

In the S. V. Lebedev Laboratory at the Leningrad State University it was established that increase of polarity of the solvent (addition of ethyl alcohol to pentane in the system being hydrogenated) leads to a rise in the degree of hydrogenation of diallyl over palladium-on-calcium carbonate from 84 to 100%. It may be expected that by a suitable selection of catalyst and solvent the process of hydrogenation of rubber might be realized with greater facility and with a smaller consumption of catalyst [5].

On the basis of the foregoing considerations, it was resolved to investigate the process of hydrogenation of rubber in a solvent whose chemical character differed from heptane. The solvent chosen was 2,2-dimethyldioxane-1,5 (DMD). For removal of peroxy compounds, DMD was kept for 24 hours in presence of hydroquinone and distilled in presence of hydroquinone in a nitrogen atmosphere; it then had b.p. 133-134° n_D^{20} 1.4230.

Hydrogenated butadiene rubber was insoluble in DMD; during hydrogenation in presence of palladium-on-calcium carbonate, the hydrogenated product therefore remained on the surface of the solvent. A 30-fold amount of catalyst was needed to hydrogenate the whole of the initial rubber in DMD. Part of the original rubber remained in solution when insufficient catalyst was used; this could be judged by data for determination of the degree of unsaturation, the content of internal double bonds, the refractive index and the relative viscosity of the benzene solution of the rubber recovered from solution.

In order to evaluate the selectivity of the hydrogenation of the double bonds of the rubber in DMD, the rubber was hydrogenated to the extent of 50%. Results showed, however, that although an adequate amount of catalyst was used, not all the rubber was 50% hydrogenated. Rubber washed out from the catalyst with benzene had 8% unsaturation; rubber isolated from solution had 84.4% unsaturation.

Results obtained with DMD are presented in the table below.

Characteristics of Specimens of Hydrogenated Butadiene Rubber Obtained with Palladium-on-Calcium Carbonate Catalyst in 2,2-Dimethyldioxane-1,5

Specimen number	Percent hydrogen added	Rubber specimen	Unsaturation (%)	Percent of internal double bonds	n_D	Relative viscosity (0.08% benzene solution)	Vitrification temperature
—	0	—	86.2	38.0	1.5120	1.310	—60.0°
1	56.4	From solution	—	36.5	1.5065	1.315	—
2	22.9	From solution	84.4	37.0	1.5120	1.313	—
		From catalyst	8.0	9.5	1.4820	1.154	—
3	81.3	From catalyst	7.6	—	1.4824	1.185	—71.7
4	50	From solution	84.1	—	1.5118	1.320	—
		From catalyst	2.7	—	1.4802	1.148	—

In the case of hydrogenated butadiene rubber obtained with palladium-on-calcium carbonate catalyst in DMD (washed out of the catalyst with benzene) the same relation between degree of hydrogenation and properties is observed as that established for hydrogenated rubber obtained in heptane with the same catalyst: fall in relative viscosity of benzene solutions, fall in refractive index and lowering of the temperature of vitrification of the rubber with increasing degree of hydrogenation. The absence of outer double bonds in hydrogenated rubber with 8% unsaturation (judging by data for the internal double bonds) indicates that the outer double bonds are hydrogenated more rapidly than the internal bonds.

It is noteworthy that in the case of hydrogenated rubber with 8% unsaturation, obtained in DMD, the percentage of residual internal double bonds is about the same as the unsaturation and amounts to 9.5%, whereas in the case of hydrorubber obtained in heptane and with a percentage unsaturation of 11.6% [5] the percentage of residual internal double bonds is 5.5%. The difference in selectivity of the hydrogenation of double bonds in rubber which was detected during hydrogenation in heptane and DMD is evidently due to the heterogeneity of the hydrorubbers examined. It is very probable that the product of hydrogenation of rubber (a high-molecular, unsaturated hydrocarbon comprising a mixture of polymer-homologs) is not, strictly speaking, homogeneous, and that the degree of unsaturation of its individual molecules may vary. The main mass of hydrogenated rubber may contain molecules of different degrees of hydrogenation and even, in some cases, molecules of unchanged rubber. In this respect the product of partial hydrogenation of rubber is an even more complex mixture of molecules of different sizes and different compositions than the original rubber.

During the hydrogenation of rubber in heptane, the hydrorubber formed at the surface of the catalyst mainly goes into the solution, as can be inferred from the degree of unsaturation found for the hydrogenated rubber and from the amount of hydrogen taken up by the rubber. In DMD, the hydrogenated rubber remains on the catalyst. Consequently, in specimens of partially hydrogenated rubber obtained in heptane, we have a mixture of hydrogenated and non-hydrogenated molecules of rubber; in specimens obtained in DMD, we have only hydrogenated molecules, since the non-hydrogenated rubber remained in solution. For this reason we obtained slightly differing results in the study of the selectivity of hydrogenation of the double bonds in heptane and in DMD.

SUMMARY

1. Experiments with allyl alcohol demonstrated the influence of the nature of the solvent on the speed and degree of hydrogenation of an unsaturated organic compound on palladium-on-calcium carbonate catalyst.

2. Butadiene rubber was hydrogenated on palladium-on-calcium carbonate in 2,2-dimethyldioxane-1,5 (DMD), and specimens of hydrorubber insoluble in that solvent were obtained.

3. The same relation between degree of hydrogenation and properties was found for hydrorubber obtained with palladium-on-calcium carbonate catalyst in 2,2-dimethyldioxane-1,5 as had been established for hydrorubber obtained in heptane with the same catalyst: fall in relative viscosity of benzene solutions, lowering of refractive index, and fall in the temperature of vitrification of the rubber with increasing degree of hydrogenation.

4. The selectivity of hydrogenation of the outer double bonds of butadiene rubber when hydrogenated in 2,2-dimethyldioxane is more clearly manifested than in the case of hydrogenation in heptane.

LITERATURE CITED

[1] S. A. Fokin, J. Russ, Phys. Chem. Soc. 40, 276 (1908).

[2] Yu. S. Zalkind and L. V. Pishchikova, J. Russ, Phys. Chem. Soc. 46, 1527 (1914).

[3] K. A. Taipale, J. Russ. Phys. Chem. Soc. 57, 485 (1925).

[4] L. I. Antropov and G. I. Pochekaeva, J. Phys. Chem. 27, 1710 (1953).

[5] A. I. Yakubchik and G. N. Gromova, J. Gen. Chem. 26, 1381 (1956) (T. p. 1557).*

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* T. p. = C. B. Translation patination.

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THE CHEMICAL STRUCTURE OF THE AUTOPOLYMER OF BUTADIENE

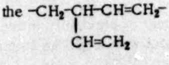
A. I. Yakubchik and A. I. Spasskova

Many investigators have observed that butadiene and its homologs are transformed during storage into white, friable polymers, insoluble in common organic solvents and possessing limited swelling capacity [1]. Formation of a friable butadiene polymer is observed in the large-scale production of butadiene and butadiene-styrene synthetic rubbers [2].

Our objective in the present work was the study of the structure of this polymer of butadiene in order to elucidate the factors responsible for the lack of rubber-like properties. Friable butadiene polymer was prepared by keeping butadiene in sealed ampoules in a nitrogen atmosphere at 15-20°. These polymerization conditions result in formation of butadiene dimer and two high-molecular polymers of which one is rubbery and soluble in chloroform, benzene and other solvents, while the other is friable, insoluble in organic solvents, and constitutes the main mass (85-90%) of product; we shall call the friable polymer the spongy butadiene polymer in the present paper. Among the products of ozonolysis of the spongy butadiene polymer were found: succinaldehyde, formic acid and formaldehyde; in the form of methyl esters were detected: succinic acid, butane-1,2,4-tricarboxylic acid, and hexane-1,x,y,6-tetracarboxylic acid. Succinic acid and succinaldehyde are formed on ozonolysis from those portions of the macromolecule of spongy butadiene polymer in which the butadiene molecules are linked in the -1,4-1,4- position [3].[•] Formaldehyde, formic acid and butane-1,2,4-tricarboxylic acid are formed from -1,4-1,2-1,4- portions. The isomeric hexane-1,x,y,6-tetracarboxylic acids, also formic acid and formaldehyde, are formed from -1,4-1,2-1,2-1,4- fragments [3]. Results of investigation of the products of ozonolysis of spongy butadiene polymer are set forth in Table 1.

TABLE 1[••]

Products of ozonolysis	Weight (in g)	Percent of carbon skeleton of polymer in the substance	Percent of butadiene molecules linked in positions	
			1.4	1.2
Succinic acid	45.20	43.4	43.4	–
Succinaldehyde	1.90	2.1	2.1	–
Dimethyl succinate	13.66	10.5	10.5	–
Trimethyl butane-1,2,4-tricarboxylate	22.16	21.4	10.7	10.70
Tetramethyl ester of hexane-1,x,y-6-tetracarboxylic acid	8.66	6.1	2.0	4.06
Total	91.58	83.5	68.7	14.76

[•] The $CH_2{-}CH{=}CH{-}CH_2{-}$chain is arbitrarily designated 1,4; the  $-CH_2-\underset{\displaystyle CH=CH_2}{\underset{|}{CH}}-CH=CH_2-$ is 1,2.

[••] Calculated on 50 g of ozonized polymer.

In the study of the products of ozonolysis of spongy butadiene polymer, 83.5% of the structure of the carbon skeleton was established: 56.0% of the butadiene molecules are linked in the -1,4-1,4- position; 21.4% are made up of -1,4-1,2-1,4- chains, and 6.1% of $-1.4-(1,2)_2-1,4-$ portions. 22.8% of chains with external double bonds were found in spongy butadiene polymer. This polymer has the same structure as the rubbery butadiene polymers. The physical properties of the spongy polymer may be governed by the conditions of its formation. A necessary condition for the formation of spongy polymer must be considered to be [4] the presence in the monomer of an insoluble nucleus* as well as of a large number of groups (α-methylene groups) linked to the nucleus and capable of initiating the growth of chains and participating to a small extent in chain-breaking. Owing to the presence in the active nucleus of a large number of radicals, a large number of macromolecules linked with one another by an insoluble nucleus can grow from a small number of molecules of nucleus.

The insolubility of the spongy polymer may be explained by the insolubility of the nucleus; its friability may be accounted for by the conditions of growth of the nucleus. The latter first swells, then cracks and, finally, breaks up into thin granules. The size reduction of the growing spongy polymer is the result of the growth taking place throughout the whole mass of the nucleus [5].

The relative content of chains with internal and external double bonds is determined in the soluble butadiene polymer, isolated from the butadiene autopolymer in very small quantity (4.0 g), by oxidation with benzoyl hydroperoxide.

EXPERIMENTAL

Butadiene autopolymer is prepared by slow polymerization of butadiene in sealed ampoules in a nitrogen atmosphere in the light at 15-20°. It is a white, friable mass, readily oxidizing in the air; all work with it was therefore performed in a nitrogen atmosphere. From 60 g autopolymer, 5.9 g (9.8%) butadiene dimer was distilled off at 15-20 mm and 40°.

B.p. 65-66° at 100 mm, d_4^{20} 0.8312, n_D^{20} 1.4650, MR_D 35.90; Calc. 36.03.
Found %: C 98.53; H 11.1. C_8H_{12}. Calculated %: C 88.89; H 11.11.
Found for ethenyl-1-cyclohexene-3: d_4^{20} 0.8320 [6].

Chloroform extraction of the butadiene autopolymer, after separation of the butadiene dimer, gave 4 g (6.4%) of rubbery polymer; the remaining autopolymer (to be designated the spongy polymer) is a white, friable substance, substantially insoluble in common organic solvents and only swelling in them to a slight extent.

Found %: C 84.53, 84.70; H 10.74, 10.98. $(C_4H_6)_x$. Calculated %: C 88.89; H 11.11.

Ozonization of the spongy polymer of butadiene was effected at -30° with oxygen containing 5-6% ozone in an apparatus ensuring constant concentration of ozone [7]. Only 37% of the polymer was ozonized when the polymer was in the form of a suspension in chloroform. Ozonization in chloroform gives an insoluble ozonide which remains on the surface of the polymer and hinders its further ozonization. This ozonide resinifies to a considerable extent when heated with water. Ozonization goes to completion if the spongy polymer is ozonized in suspension in ethyl acetate, and a colorless, transparent solution of ozonide is formed. After distillation of the ethyl acetate, the ozonide remains in the form of a colorless, transparent, very viscous substance. This ozonide is decomposed by water without resinification.

The ozonide, destined for elementary analysis, was purified by dissolving in ethyl acetate and precipitating from the solution with ligroine (this procedure was applied three times).

Found %: C 45.89, 45.79; H 6.90, 6.90; O 47.21, 47.31. $(C_4H_6O_3)_x$ Calculated %: C 47.06; H 5.88; O 47.06.

The deviations of the experimental from the calculated values are within the usual limits of error for ozonides; the ozonide of butadiene spongy polymer may therefore be assigned the formula $(C_4H_6O_3)_x$.

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* Formed from the polymer or previously introduced into it. Breitenbach is of the opinion that long, entangled thread-like macromolecules with a gellike structure are formed in the first stage of development of spongy polymer.

Products of ozonolysis were prepared for investigational purposes from 50 g of the spongy polymer (containing 42.4 g carbon) in ethyl acetate at -30°; 1.5-2 g polymer was ozonized in each experiment. The ozonides were decomposed by heating with water. The aqueous solutions of the products of decomposition of ozonides from the different experiments were combined and the water was driven off, at first at atmospheric pressure (to 1/3 of the original volume) and later at 150-100 mm. The product of decomposition of the ozonide was a crystalline substance permeated with a viscous liquid. The crystals were separated with diethyl ether and recrystallized from hot water; m.p. 183°; the melting point of the mixture of the substance with succinic acid was also 183°. The neutralization equivalent of the crystalline acid was 59.2; its anhydride had m.p. 120°. From the products of ozonolysis was isolated 33.7 g succinic acid, containing 13.7 g carbon. Succinaldehyde was detected by the pyrrole test in the distillate coming over with the water. The amount of succinaldehyde in the distillate was determined from the weight of its phenylhydrazone isolated from the solution. The phenylhydrazone melted at 124-125° (from alcohol). The literature gives m.p. 125° [8] and 124-125° [9] for succinaldehyde phenylhydrazone. The aqueous distillate was found to contain 1.9 g succinaldehyde, equivalent to 1.06 g carbon. 56.1 g viscous products of ozonolysis was collected; its carbon content was 44.9%. The 56.1 g viscous products of ozonolysis contained 25.2 g carbon. Properties of aldehydes and acids were detected; evidently a mixture of aldehydes, aldehydo acids and acids is involved. The mixture was oxidized with acetyl hydroperoxide. The latter was prepared from acetic anhydride and concentrated aqueous hydrogen peroxide in presence of sulfuric acid [10]. 91.6% of the products of ozonolysis (containing 22.6 g carbon) was oxidized. 2.7 g carbon was lost in the oxidation. Yield of acids 89.4%. The product of oxidation was a white, crystalline mass permeated with a colorless, viscous substance. The crystals were separated with ethyl acetate. In this way 10.5 g succinic acid was isolated and melted at 183° after recrystallization; 37.7 g viscous acids was also collected and converted by the action of an ethereal solution of diazomethane into methyl esters of carboxylic acids. The acid esters were separated from the full methyl esters by washing many times with 5% aqueous sodium bicarbonate solution. The full methyl esters were dried with fused sodium bisulfate, and the ethyl ester was distilled off. 28.2 g full methyl esters was obtained. 4.2 g acid methyl esters was extracted with diethyl ether from the acidified sodium bicarbonate solution. The mixture of methyl esters was fractionated from a flask with a long column; results of fractionation are given in Table 2.

TABLE 2

Fraction number	Boiling point at 2 mm pressure	Weight (in g)
1	58-61°	8.2
2	127-130	1.7
3	130-133	11.6
4	180-190	5.2
Residue in flask.		1.5

TABLE 3

Fraction number	Weight of methyl esters (in g)	
	obtained from fractionation of 28.2 g esters	calculated for 50 g of ozonized polymer
1	8.2	13.66
2	13.3	22.16
3		
4	5.2	8.66
Residue.	1.5	2.66

76.3% of the acids (15.7 g carbon) was esterified to give 28.2 g methyl esters instead of the theoretical amount of 38.1 g, i.e. 73.1%. 4.2 g acid esters was isolated. The losses of esters were 5.7 g. The weight of these esters from the products of decomposition of the ozonide of 50 g spongy butadiene polymer was calculated on the basis of the weight of the methyl esters (Table 3).

Results of the investigation of the methyl esters of the carboxylic acids obtained from the product of ozonization of the spongy polymer of butadiene are presented in Table 4.

Investigation of the methyl esters of the carboxylic acids showed that the first fraction was dimethyl succinate; the analyses of the second fraction indicate that it is substantially the trimethyl ester of butane-1,2,4-tricarboxylic acid; it apparently contains a small proportion of the previous fraction; the third fraction is the trimethyl ester of butane-1,2,4-tricarboxylic acid; the fourth fraction corresponds to the tetramethyl ester of hexane-1,x,y,6-tetracarboxylic acid.

TABLE 4

Fraction number	Found				d_4^{20}	n_D^{20}	MR_D	Formula	Calculated				
	% C	% H	M	Saponification equivalent					% C	% H	M	Saponification equivalent	MR_D
1	48.9	6.89	148.5	—	—	—	—	$C_6H_{10}O_4$ *	49.31	6.90	146	73	32.21
1	49.1	6.89	146.2	73.1	0.1202	1.4190	32.80						
2	—	—	208.9	—	—	—	—	—	—	—	—	—	—
2	49.77	6.64	204.0	68.1	—	—	—	—	—	—	—	—	—
3	50.86	6.64	229.8	76.6	—	—	—	$C_{10}H_{16}O_6$ *	51.72	6.95	232	77	51.63
3	50.70	6.67	235.8	78.6	1.1811	1.4420	51.96						
4	52.82	6.31	320.4	80.1	—	—	—	$C_{14}H_{22}O_8$ *	52.82	6.91	318	79.5	70.19
4	52.71	6.51	319.6	79.9	1.2195	1.4643	70.00						

* Literature data: for $C_6H_{10}O_4$ n_D^{20} 1.4192 [11]; d_4^{20} 1.12077 [12]; for $C_{10}H_{16}O_6$ n_D^{20} 1.4446 [11]; for $C_{14}H_{22}O_8$ n_D^{20} 1.4643 [11].

The ozonized polymer contained 42.4 g carbon. The isolated succinic acid, succinaldehyde, formic acid and formaldehyde represented 19.5 g of the carbon of the polymer. The isolated and characterized methyl esters of carboxylic acids contained 15.7 g carbon. In all, 35.2 g (83 %) of the carbon of the polymer was accounted for. The loss of carbon was 7.2 g; of this, 2.7 g was lost during oxidation of the product of ozonolysis with acetyl hydroperoxide; the remaining 4.5 g was in the uninvestigated acid methyl esters and in the residue after fractionation of the full methyl esters of the carboxylic acids.

Determination of chains with external double bonds in butadiene spongy polymer. The method consists in quantitative determination of the formic acid and formaldehyde in the products of ozonolysis of the polymer [13]. This is usually carried out in chloroform. Since the spongy polymer does not undergo ozonization in chloroform, the reaction was carried out in ethyl acetate, the latter solvent, however, is less stable to ozone. In the first place, therefore, comparative determinations were made of formic acid and formaldehyde in the products of decomposition of the ozonide of butadiene rubber after ozonization in chloroform and in ethyl acetate. On the basis of these data the percentage of chains with external double bonds was calculated. Results are set forth in Table 5 and show that reliable results are also obtained with ethyl acetate as the solvent during ozonization.

TABLE 5

Weight of ozonized rubber (in g)	Solvent for ozonization	Percent carbon in the ozonized rubber	Percent of chains with external double bonds in the rubber
2.5	Chloroform	87.67	34.68
2.5	Ethyl acetate	87.67	34.36

For the purpose of determination of the chains with external double bonds, 2.3 g spongy polymer was ozonized in ethyl acetate. Formic acid and formaldehyde were determined in the aqueous solution of the products of decomposition of the ozonide, and the percentage of chains with external double bonds was calculated (22.8%).

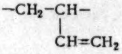
Determination of the unsaturation of the chloroform-soluble butadiene polymer isolated from butadiene autopolymer. The method described by A. A. Vasilyev [14] was used, based on the reaction of rubber with iodine bromide. Results are presented in Table 6.

TABLE 6

Weight of polymer (g)	Iodine number found without allowance for substitution	Degree of unsaturation of the polymer without allowing for substitution (%)	Iodine number found with allowance for substitution	Unsaturation of the polymer with allowance for substitution (%)
0.0964	435.8	92.7	407.0	80.6
0.0954	435.1	92.7	413.0	86.8

Determination of the internal double bonds in the chloroform-soluble butadiene polymer. The method of Prilezhaev [15] was applied. This is based on the different velocities of oxidation by benzoyl hydroperoxide of olefinic bonds with different degrees of substitution.

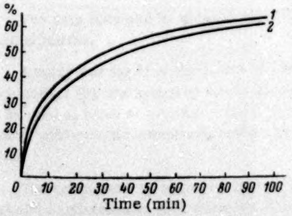
Butadiene rubbers contain $-CH_2-CH{=}CH-CH_2-$ chains (internal double bonds) and



$$\begin{array}{l}-CH_2-CH-\\ \qquad\quad |\\ \qquad\; CH{=}CH_2\end{array}$$

chains (external double bonds). The double bond in the chain containing an internal double bond is oxidized more rapidly than that in the chain with an external double bond. The percentage of internal double bonds is determined from the kinetic curve of oxidation of the rubber with benzoyl hydroperoxide [16].

Oxidation of the polymer with benzoyl hydroperoxide was carried out in a thermostat at 20°. To 50 ml 0.2 N solution of polymer in chloroform was added 50 ml 0.2 N solution of benzoyl hydroperoxide in chloroform. At definite time intervals 5 ml samples were withdrawn for determination by the iodometric method of the amount of benzoyl hydroperoxide reacted. Parallel samples were taken (5 ml each) from a solution containing only benzoyl hydroperoxide in order to determine the amount of hydroperoxide decomposed. For the purpose of calculation of the percentage of chains with internal double bonds in the polymer in question, oxidation was effected with benzoyl hydroperoxide of butadiene dimer containing double bonds of the same type as those in butadiene polymers. The butadiene dimer was oxidized under the same conditions and with identical ratios of concentrations of the solutions of dimer and hydroperoxide and at the same temperature as in the oxidation of the dissolved butadiene polymer. The curves of rate of oxidation of butadiene dimer and of soluble polymer are plotted in the diagram in which the abscissas represent the times in minutes and the ordinates the percent of reacted substance. From the curve we find the time in the course of which 50% of the butadiene dimer was oxidized (i.e. the double bond in the ring), and we assume that the internal double bonds of the butadiene polymer also reacted in the same time. It follows from the diagram that the chloroform-soluble polymer separated from the autopolymer contains 53.5% of chains with internal double bonds and 33.3% of chains with external double bonds.



Curves of velocity of oxidation of soluble butadiene polymer (1) and of butadiene dimer (2) by benzoyl hydroperoxide

SUMMARY

1. The chemical structure of spongy butadiene polymer, obtained at 15-20°, was examined by the ozonolysis method.

2. The percent of chains with external double bonds in the spongy polymer was found to be 22.8%.

3. The spongy polymer of butadiene is composed, like the rubbery polymers, of chains with external and internal double bonds.

4. It was established that parts of the molecule of spongy polymer have the same structure as the rubbery butadiene polymers: -1, 4-1, 4-; -1,4-1,2-1, 4-; -1, 4-1, 2-1, 2-1, 4-.

5. A chloroform-soluble rubber-like polymer was separated from the butadiene autopolymer. The degree of unsaturation of the chloroform-soluble polymer was determined (86.7%), also the relative content of internal and external double bonds.

LITERATURE CITED

[1] L. L. Kondakov, Synthetic Rubber (1912); S. V. Lebedev, J. Russ. Chem. Soc. 42, 949 (1910); 43, 1124 (1911); 45, 1249 (1913); Harries, Investigations on Natural and Synthetic Rubber Varieties (1919).

[2] G. G. Koblyansky and K. B. Piotrovsky, Trans. All-Union Synthetic Rubber Research Institute 2, 23 (1948); M. Kharash and Nudenberg, Ind. Eng. Chem. 39, 830 (1947).

[3] A. I. Yakubchik, Academician S. V. Lebedev (1954).

[4] E. Immergut, Makromol. Chem. 10, 4790 (1953); J. Breitenbach and H. Mark, Chemie 78, 293 (1948).

[5] Welch, Ind. Eng. Chem. 39, 826 (1947); Devins and Winkler, Can. J. Research 26, 356 (1948); Miller, J. Polymer Sci. IX, 5, 453 (1952).

[6] S. V. Lebedev, Investigations on Diethylenic Hydrocarbons (1913).

[7] A. I. Yakubchik N. G. Kasatkina and P. Pavlovskaya, J. Gen. Chem 25, 1473 (1955) (T.p. 1419).*

[8] Harries, Ber. 35, 1184 (1902).

[9] B. Zanetti, Ber. 22, 1974 (1889).

[10] B. A. Arbuzov, Investigations on Isomeric Transformations of Bicyclic Hydrocarbons and Their Mixtures (1936).

[11] N. Rabjohn and G. Bryan, J. Am. Chem. Soc. 69, 314 (1947).

[12] Emery, Ber. 22, 3185 (1889).

[13] A. I. Yakubchik, A. A. Vasilyev and V. M. Zhabina, J. Appl. Chem. 17, 3, 107 (1944).

[14] A. A. Vasilyev, J. Gen. Chem. 17, 923 (1947).

[15] N. Prilezhaev, Organic Peroxides and Their Application to the Oxidation of Unsaturated Compounds (1912).

[16] Kolthoff, J. Polymer Sci. II, 2, 199, 202, 206 (1947); A. Saffer and B. Johnson, Ind. Eng. Chem. 40, 3, 538 (1948).

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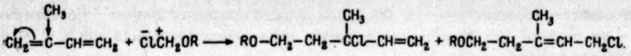
* T. p. = C. B. Translation Pagination.

ADDITION OF α-HALOETHERS TO ISOPRENE

A. N. Pudovik and N. Altunina

In a series of previous investigations we made a detailed study of the addition of α-haloethers of the type of $CH_2Cl—O—R$ and $CH_3CHCl—O—R$ [1] to butadiene.. In all cases 1,2- and 1,4- products of addition (isomeric alkoxychloropentenes and alkoxychlorohexenes) were isolated. On the basis of a study of the catalytic isomerization of the isomeric alkoxychloropentenes, it was established that α-haloethers add on to butadiene to the extent of 65-77% in the 1,2- position and to the extent of 23-35% in the 1,4- position. Continuing the work by studying the addition of α-haloethers to isoprene, we attempted to apply the procedure that we had developed for butadiene. It was found, however, that the reactions with isoprene in presence of zinc chloride proceed with extreme violence; in spite of cooling of the reaction mixture with freezing mixture, the thick-walled glass flasks could not withstand the pressure developed. Only a small amount of high-boiling products, but much resin, was obtained if the reactions were conducted in a cooled flask and with slow addition of the haloether while stirring. Satisfactory results were obtained by working in ether solution with cooling. Two addition products were obtained in each case on addition of chloromethyl methyl, chloromethyl ethyl and chloromethyl butyl ethers to isoprene.



$$CH_2{=}\overset{CH_3}{\overset{\downarrow}{C}}{-}CH{=}CH_2 + \overset{-}{Cl}\overset{+}{C}H_2OR \longrightarrow RO{-}CH_2{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}Cl{-}CH{=}CH_2 + ROCH_2{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_2Cl.$$

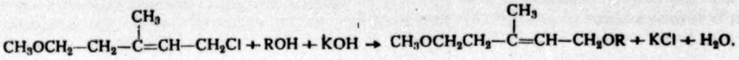
The total yield of isomeric alkoxychloroisohexenes was 30-37%. Considerably more primary chloride than tertiary chloride was obtained in all cases. Formaldehyde was identified among the products of ozonization of 1-methoxy-3-chloro-3-methylpentene-4. Oxidation of 1-ethoxy-3-methyl-5-chloropentene-3 with potassium permanganate gave chloroacetic acid.

The susceptibility to isomerization of the isomeric alkoxy chloroisohexenes is very much greater than that of the isomeric alkoxychloropentenes. Alkoxychloro-isohexenes are fairly stable at room temperature; the refractive index (n_D^{20}) of 1-methoxy-3-chloro-3-methylpentene-4 only changed by 0.0006 after a month; at 100° the equilibrium state is reached after 4 hours. The kinetic curves of isomerization of the isomeric methoxychloroisohexenes and ethoxychloro-isohexenes are plotted in Figures 1 and 2. The compositions at equilibrium are 16.9% 1-methoxy-3-chloro-3-methylpentene-4 and 83.1% 1-methoxy-5-chloro-3-methylpentene-3; 9.4% 1-ethoxy-3-chloro-3-methylpentene-4 and 90.6% 1-ethoxy-5-chloro-3-methylpentene-3.

The data obtained by thermal isomerization confirm the correctness of the proposed structure of the unsaturated chlorides.

A study was made of the action of alcoholic alkali on 1-methoxy-3-methyl-5-chloropentene-3. As we had shown earlier [2], the action of alcoholic alkali is specific for primary and secondary haloallyl compounds and can be used as proof of structure. Good yields of the corresponding ethers are obtained with the primary haloallyl isomers, while dienic compounds and a mixture of isomeric ethers are obtained with secondary haloallyl compounds.

The corresponding diethers were obtained in yields of 55-60% by the action of potassium hydroxide in methyl, ethyl and butyl alcohols on 1-methoxy-3-methyl-5-chloropentene-3:



$$CH_3OCH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2Cl+ROH+KOH\rightarrow CH_3OCH_2CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2OR+KCl+H_2O.$$

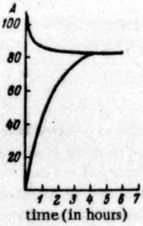


Figure 1. Isomerization curves of methoxychloro-isohexenes.
A) Content of 1-methoxy-3-methyl-5-chloropentene-3 (in %).

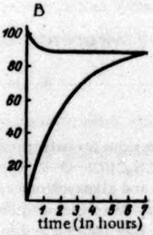


Figure 2. Isomerization curves of ethoxychloro-isohexenes.
B) Content of 1-ethoxy-3-methyl-5-chloropentene-3 (in %).

Reaction of 1-butoxy-3-methyl-5-chloropentene-3 with KOH in methanol solution gave a 51% yield of 1-butoxy-5-methoxy-3-methylpentene-3. One of the prepared unsaturated diethers – 1,5-dimethoxy-3-methylpentene-3 – was oxidized with potassium permanganate, and a methoxyacetic acid with b. p. 90-94° at 11 mm and n_D^{20} 1.4180 was isolated.

EXPERIMENTAL

Addition of chloromethyl ether to isoprene. 100 g chloromethyl ether was added to 102 g isoprene, 100 ml dry ether and 2 g freshly fused, pulverized zinc chloride contained in a three-necked flask of 0.5 liter capacity. The chloromethyl ether was introduced over a period of 3 hours. During the addition the flask was cooled with tap water and the reaction mixture was continuously stirred with a mechanical stirrer. The rate of addition of the haloether was regulated in such a fashion that the temperature of the reaction mixture did not rise above 10°. The reaction mixture was thereupon treated with water, the ether layer was dried with calcium chloride, the ether was driven off, and the residue was fractionated in vacuum. The initial fractionation in a Widmer column gave 17.28 g of a fraction with b. p. 40-72.5° at 17 mm, 48.3 g of a fraction with b. p. 68-72° at 10 mm, and 64.8 g of higher boiling residue. Redistillation of the two fractions gave 8.1 g of 1-methoxy-3-chloro-3-methylpentene-4 (I) and 48.5 g of 1-methoxy-3-methyl-5-chloropentene-3 (II).

(I) B. p. 48.5-49.5° at 11 mm, d_4^{20} 0.9614, n_D^{20} 1.4462, MR_D 41.16; calc. 40.57.
Found %: Cl 23.84. $C_7H_{13}OCl$. Calculated %: Cl 23.90.
(II) B. p. 71-72° at 11 mm, d_4^{20} 0.9900, n_D^{20} 1.4610, MR_D 41.16; calc. 40.57.
Found %: Cl 23.58. $C_7H_{13}OCl$. Calculated %: Cl 23.90.

Ozonization of 1-methoxy-3-methyl-3-chloropentene-4. A stream of ozonized oxygen was passed for 16 hours through a solution of 5 g 1-methoxy-3-methyl-3-chloropentene-4 in 40 ml carbon tetrachloride while cooling with freezing mixture. The carbon tetrachloride was distilled off and ether was poured on to the residual oily ozonide which was then left at room temperature for 24 hours. The ozonide was then decomposed by boiling with 50 ml water; formaldehyde was identified in the distillate by the β-naphthol test; the condensation product had m. p. 192°.

Action of KOH on 1-methoxy-3-methyl-5-chloropentene-3 in methanol solution. To a solution of 15 g KOH in 100 ml methanol was gradually added 20 g of 1-methoxy-3-methyl-5-chloropentene-3. The reaction mixture was heated for 1 hour on a water bath, the precipitated potassium chloride was filtered off, and the methanol was distilled off. Fractionation of the residue gave 10.8 g of 1,5-dimethoxy-3-methylpentene-3.

B. p. 69° at 13 mm, d_4^{20} 0.8932, n_D^{20} 1.4335, MR_D 41.96; calc. 41.70.
Found %: C 66.71; H 11.09. $C_8H_{16}O_2$. Calculated %: C 66.67; H 11.12.

Oxidation of 1,5-dimethoxy-3-methylpentene-3 with potassium permanganate. 6 g of the product was dissolved in 300 ml water and 13.2 g permanganate was added with constant stirring, the temperature being held at not higher than 10-12°. The precipitated manganese dioxide was filtered off, treated with hot water and again filtered. The wash liquors were evaporated to 30-40 ml, the residue was treated with sulfuric acid (1 : 2) until acidic, extracted with ether, and dried with calcium chloride. The ether was then distilled off, and the residue was fractionated to give 2.1 g methoxyacetic acid.

B. p. 92-94° at 11 mm, n_D^{20} 1.4180.
Found %: C 39.62; H 6.83. $C_3H_6O_3$. Calculated %: C 40.00; H 6.66.
Literature data: b. p. 96.5° at 13 mm, n_D^{20} 1.4168.

Action of KOH on 1-methoxy-3-methyl-5-chloropentene-3 in ethanol solution. To a solution of 15 g KOH in 100 ml ethanol was added 20 g of the chloride. Fractionation of the reaction mixture gave 11.7 g 1-methoxy-5-ethoxy-3-methylpentene-3.

B. p. 80° at 13 mm, d_4^{20} 0.8810, n_D^{20} 1.4350, MR_D 46.78; calc. 46.58.
Found %: C 67.95; H 11.19. $C_9H_{18}O_2$. Calculated %: C 68.34; H 11.38.

Action of KOH on 1-methoxy-3-methyl-5-chloropentene-3 in butyl alcohol solution. 10 g KOH was dissolved in 50 ml n-butyl alcohol, and 10 g of the chloro compound was added. Yield 5.1 g 1-methoxy-5-butoxy-3-methylpentene-3.

B. p. 102-103° at 11 mm, d_4^{20} 0.8736, n_D^{20} 1.4395, MR_D 55.98; calc. 55.83.
Found %: C 70.71; H 11.67. $C_{11}H_{22}O_2$. Calculated %: C 70.98; H 11.82.

Thermal isomerization of isomeric methoxy- and ethoxy-chloroisohexenes. 2-3 g of the chloride was sealed into a glass ampoule and placed in a boiling water bath. The progress of isomerization was followed by measurements of the refractive index. Results are plotted in Figures 1 and 2.

Addition of chloromethyl ethyl ether to isoprene. In the course of 3 hours 58 g chloromethyl ethyl ether was added to an ethereal solution of 45 g isoprene containing 1 g freshly fused, pulverized zinc chloride while cooling with tap water and with continuous stirring. Throughout the experiment the temperature of the reaction mixture was not allowed to rise above 10°. Several fractionations of the reaction mixture gave 6.6 g 1-ethoxy-3-methyl-3-chloropentene-4 (III) and 26.9 g 1-ethoxy-3-methyl-5-chloropentene-3 (IV). Residue 8 g.

(III) B. p. 57° at 13 mm, d_4^{20} 0.9475, n_D^{20} 1.4425, MR_D 45.39; calc. 45.19.
Found %: Cl 21.37. $C_8H_{15}OCl$. Calculated %: Cl 21.85.
(IV) B. p. 77-78° at 12 mm, d_4^{20} 0.9685, n_D^{20} 1.4552, MR_D 45.52; calc. 45.19.
Found %: Cl 21.77. $C_8H_{15}OCl$. Calculated %: Cl 21.85.

Oxidation of 1-ethoxy-3-methyl-5-chloropentene-3 with potassium permanganate. To a solution of 8 g product in 300 ml water was added 15.5 g potassium permanganate. The reaction was then carried out as described above to give 1.3 g of chloroacetic acid with b. p. 94-96° at 12 mm.

Found %: Cl 37.03. $C_2H_3O_2Cl$. Calculated %: Cl 37.56.
Literature data: b. p. 104° at 20 mm.

Addition of chloromethyl butyl ether to isoprene. Reaction was effected between 80 g chloromethyl butyl ether and 54 g isoprene in ethereal solution in presence of 1 g zinc chloride, using the procedure described above. Several fractionations in a Widmer column gave 6.1 g dibutyl formal with b. p. 70° at 13 mm and n_D^{20} 1.4065, 11.4 g 1-butoxy-3-methyl-3-chloropentene-4 (V) and 22.9 g 1-butoxy-3-methyl-5-chloropentene-3 (VI).

(V) B. p. 91-93° at 9 mm, d_4^{20} 0.9303, n_D^{20} 1.4450, MR_D 54.51; calc. 54.42.
Found %: Cl 19.36. $C_{10}H_{19}OCl$. Calculated %: Cl 18.63.
(VI) B. p. 102-103° at 11 mm, d_4^{20} 0.9530, n_D^{20} 1.4561, MR_D 54.13; calc. 54.42.
Found %: Cl 18.63. $C_{10}H_{19}OCl$. Calculated %: Cl 18.63.

Action of KOH on 1-butoxy-3-methyl-5-chloropentene-3 in methanol solution. To a solution of 10 g KOH in 50 ml methanol was added 10 g chloride. The reaction mixture was heated on a water bath for 1 hour and then worked up by the procedure of the preceding experiment. Yield 6.5 g 1-methoxy-5-butoxy-3-methylpentene-3.

B. p. 97-98° at 11 mm, d_4^{20} 0.8734, n_D^{20} 1.4380, MR_D 55.88; calc. 55.83.
Found %: C 70.84; H 11.91. $C_{11}H_{22}O_2$. Calculated %: C 70.98; H 11.83.

SUMMARY

1. A method was developed for the addition of α-haloethers to isoprene. The reaction was conducted in presence of zinc chloride in ethereal solution, with cooling and stirring.

2. It was shown that α-haloethers add on to isoprene in the 1,2- and 1,4- positions. The total yield of addition products is 30-37%, but the amount of primary chloride formed is several times greater than that of tertiary chloride.

3. The thermal isomerization of the isomeric methoxy- and ethoxy-chloroisohexenes was studied. In the equilibrium state the primary chlorides constitute respectively 83.1 and 90.6%.

4. The corresponding diethers are formed by the action of alcoholic alkali upon the primary methoxy- and ethoxy-chloroisohexenes.

LITERATURE CITED

[1] A. N. Pudovik and B. A. Arbuzov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1946, 427; A. N. Pudovik, op. cit. 1948, 321, 529; A. N. Poduvik et al., J. Gen. Chem. 19, 279 (1949) (T.p. 241).*

[2] A. N. Pudovik and B. A. Arbuzov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1947, 377; A. N. Pudovik, op. cit. 1949, 83.

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* T.p. = C. B. Translation pagination.

INVESTIGATION OF THE MOBILITY OF THE TERTIARY BUTYL GROUP IN DERIVATIVES OF TERT.-BUTYLBENZENE BY THE METHOD OF ISOTOPIC EXCHANGE

L. M. Nazarova

The objective of the present work is the study of the mobility of the tertiary butyl group attached to an aromatic ring and the influence of polar substituents in the ring. This study was carried out by the method of exchange of tertiary butyl groups between tertiary butyl benzene and its nitro-, chloro- and hydroxy- derivatives on the one hand, and between C^{14}-labeled tert.-butyl chloride on the other hand.

The possibility of such an exchange by tert.-butyl groups is indicated by several observations of the mobility of the tert.-butyl group: in the nitration, for example, of p-acetylamino-tert.-butylbenzene with the usual mixture of nitric and sulfuric acids, it was found that the tert.-butyl group is easily replaced by the nitro group [1]. It was likewise found [2] that the action of aluminum chloride on tert.-butylacenaphthene in carbon bisulfide for 40 minutes results in migration of the tert.-butyl group from the 1- or 3- position to the 2- position relative to the acenaphthene bridge; this is followed, due to disproportionation of two molecules of 2-tert.-butylacenaphthene, by formation of 2,5-ditert.-butylacenaphthene and acenaphthene. Other similar examples could be cited.

There is likewise no doubt that the mobility of the tert.-butyl group must depend both on the nature of the substituent and on the position of the latter in the aromatic ring.

Apart from throwing light upon the problem of the influence of substituents on the mobility of side groups attached to the benzene ring, the present work is a contribution to the systematic investigation of the isotopic exchange of carbon which has hitherto been carried out inadequately and fortuitously [3]. Among the papers published in recent years, interest is attached to that of I. P. Gragerova [4] on the mobility of radicals linked with oxygen.

Exchange of tert.-butyl groups in our experiments was effected in sealed ampoules containing equimolar ratios of components. Experiments were also performed on the exchange by groups between tert.-butylbenzene labeled with C^{14} in the tertiary carbon atom and some para-derivatives of tert.-butylbenzene. Results obtained are presented in Table 1.

The data in the table show that the introduction of a negative group (NO_2, Cl) into any position of the benzene ring hinders exchange. Thus, p-nitro-tert.-butylbenzene, even in presence of catalysts ($FeCl_3$), does not exchange tert.-butyl groups with tert.-butyl chloride. Attention should be drawn in this case to the analogy with the Fries reaction in which the introduction of a nitro group also inhibits the reaction.

On the other hand, the introduction into the benzene ring of a positive group (OH) leads to appreciable exchange without catalysts. The mobility of the tert.-butyl group in o- and p-tert.-butylphenols is consistent with the exchange, noted above, of the tert.-butyl group with the nitro group during nitration of p-acetamino-tert.-butylbenzene with a mixture of nitric and sulfuric acids. It must be pointed out that the exchange is accompanied by substitution, and the greater the exchange the more hydrogen chloride and substituted products are formed.

In the case of m-tert.-butylphenol, the main product isolated after the experiment was 2,5-ditert.-butylphenol. Only a small amount of tert.-butyl chloride failed to enter into reaction.

TABLE 1

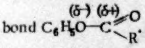
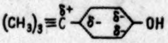
System	Conditions of Exchange		Percent exchange	Notes
	temperature	duration (in hours)		
Labeled tert.-butylbenzene and tert.-butyl chloride	120°	20	None	
Labeled tert.-butyl chloride and tert.-butylbenzene in presence of $FeCl_3$	120°	20	28.7	Separation of HCl and secondary products
Labeled tert.-butyl chloride and p-nitro-tert.-butylbenzene	120° 200°	20 20	None None	
Labeled tert.-butyl chloride and p-nitro-tert.-butylbenzene + $FeCl_3$	120°	20	None	
Labeled tert.-butyl chloride and o-nitro-tert.-butylbenzene	120°	20	None	
Labeled tert.-butyl chloride and m-nitro-tert.-butylbenzene	120°	20	None	
Labeled tert.-butyl chloride and p-chloro-tert.-butylbenzene	120°	20	None	
Labeled tert.-butyl chloride and o-chloro-tert.-butylbenzene	120°	20	None	
Labeled tert.-butyl chloride and m-chloro-tert.-butylbenzene	120°	20	None	
Labeled tert.-butyl chloride and p-tert.-butylphenol	120°	30	15.4	Separation of HCl and secondary products
Labeled tert.-butyl chloride and o-tert.-butylphenol	120°	30	21	Ditto
Labeled tert.-butyl chloride and m-tert.-butylphenol	120°	30	84.7	Ditto; analysis of the tert. butyl chloride
Labeled tert.-butylbenzene and p-amino-tert.-butylbenzene	120°	20	None	
Labeled tert.-butylbenzene and p-amino-tert.-butylbenzene	200°	20	None	
Labeled tert.-butylbenzene, p-tert.-butylphenol and $FeCl_3$ in dioxane *	120°	30	Traces of exchange	
Labeled tert.-butylbenzene, p-nitro-tert.-butylbenzene and $FeCl_3$ in dioxane *	120°	30	None	

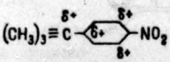
* The same results were obtained when using anhydrous aluminum chloride.

It is an interesting fact that the greatest exchange is observed with m-tert.-butylphenol. This is possibly associated with the greater increase in electronic density in the ortho- and para-positions due to the concordant orientation of both groups. Concordant orientation is lacking in o- and p-tert.-butylphenols.

In the case of tert.-butylbenzene, the exchange with tert.-butyl chloride goes at 120° only in presence of a catalyst ($FeCl_3$). Experiments on exchange of groups between tert.-butylbenzene and its derivatives showed that exchange is nil without a catalyst. Traces of exchange were observed in presence of ferric chloride or aluminum chloride only in the system tert.-butylbenzene + p-tert.-butylphenol. With rise of temperature to 220°, side reactions are observed in this system and are accompanied by separation of water and phenol as well as by considerable resinification.

The fact that in the cases studied the exchange is accompanied by substitution reactions made it impossible to study the kinetics of exchange and the mechanism of the reaction. Since, however, catalysts for this reaction are aluminum chloride and ferric chloride, it is highly probable that an ionic mechanism is involved. This hypothesis is supported by the negative result that we obtained when we attempted to perform the exchange reactions by irradiation with a mercury vapor lamp. Other evidence in favor of the ionic hypothesis is the lack (or almost complete lack) of exchange of groups between tert.-butylbenzene (in which formation of ions is unlikely) and its p-amino- and p-hydroxy- derivatives.

The cause of the mobility of the tert.-butyl group is probably the polarity of the bond between the tert.-butyl group and the benzene ring. This conclusion can be reached on the basis of the following data: The Fries rearrangement can be regarded as proceeding at the expense of the carbonium ion $\overset{+}{C}(=O)R$ with rupture of the polar bond  $C_6H_5\overset{(\delta-)}{O}-\overset{(\delta+)}{C}(=O)R$. A similar phenomenon is observed in the present investigation: in the case of o- and p-tert.-butylphenols the polarity of the bond between the carbon ring and the tertiary carbon atom of the butyl group increases due to interaction of the hydroxyl group with the ring:  At the same time the mobility of the tert.-butyl group is observed to increase. In the case of nitro-tert.-butylbenzene



the polarity of this bond increases or the bond has no polarity, which results in reduced mobility of the tert.-butyl group and the absence, in these cases, of exchange. We can similarly explain the ease of substitution of the tert.-butyl group in the case of nitration of p-acetamino-tert.-butylbenzene and the migration of the tert.-butyl group in the experiment with tert.-butylacenaphthene. . A similar increase in polarity of the bond may also account for the behavior of chlorine in p-chloronitrobenzene: notwithstanding the "aromaticity" of the chlorine (as judged by its dipole moment), it is mobile just as in aliphatic compounds. This fact had not previously been explained. But if we take into account the increase in polarity of the C—Cl bond due to interaction of the ring with the nitro group, then the mobility of the chlorine in this case becomes understandable.

EXPERIMENTAL

The present work necessitated development of a method of semimicro preparation of tert.-butyl chloride labeled with C^{14} in the tertiary carbon atom. The following method was developed: acetic acid labeled with C^{14} in the carboxyl was converted to the calcium salt; the dried salt (2.65 g) was subjected to dry distillation in a weak nitrogen stream in the apparatus sketched in Fig. 1. Traps 1 and 2 were cooled with a mixture of acetone and solid carbon dioxide. The whole of the acetone obtained by dry distillation was collected in the first trap. The acetone was then dried with potassium carbonate and distilled by gentle heating (30°) in a nitrogen stream into the other trap, immersed in a mixture of solid carbon dioxide and acetone. Yield of labeled acetone 83.6% (0.81 g).

Acetone labeled with C^{14} in the carbonyl group (0.81 g) was diluted with ordinary unlabeled acetone (pure for analysis) to a total weight of 5 g and utilized for preparation of trimethylcarbinol by the Grignard method. Synthesis was performed in the following manner: methyl magnesium iodide was prepared in the usual manner but under nitrogen, starting from 2.3 g magnesium, 5.4 ml methyl iodide and 60 ml absolute ether. The prepared solution of organomagnesium compound was forced by a nitrogen stream into flask 1 of the apparatus for synthesis of tert. butyl alcohol (Fig. 2), which had previously been purged with nitrogen. The solution of labeled acetone (5 g) in absolute ether (10 ml) was run dropwise from a separating funnel into the Grignard reagent. Flask 1 (Fig. 2) was cooled with iced water during this operation. After the whole of the acetone had been added, the mixture was boiled 15 minutes, then recooled with iced water, and decomposed at first with iced water (10 ml) and then with dilute sulfuric acid (10 ml H_2O + 2.7 ml conc. H_2SO_4). After completion of the decomposition of the organometallic compound, water was added to the contents of flask 1 until the salt had dissolved completely, and the solution was neutralized with sodium hydroxide until weakly alkaline. The reaction product was then distilled directly from the reaction flask fitted with a fractionating column packed with Fenske rings interbedded at three levels with small glass cylinders. The length of the packed column was 260 mm; its diameter was 18 mm. The ether was first distilled off and found to be free from tert.-butyl alcohol.

The fraction up to 90° (approx. 7-8 ml) was then distilled; to this fraction was added, with ice cooling, 70 ml hydrochloric acid saturated with hydrogen chloride. A layer of butyl chloride (3.76 g or 54.2% reckoned on the acetone) separated after standing for 5 days. 3.76 g of the labeled tert.-butyl chloride was diluted with inactive tert.-butyl chloride to a total weight of 40 g. Results of analysis of activity are given in Table 2.

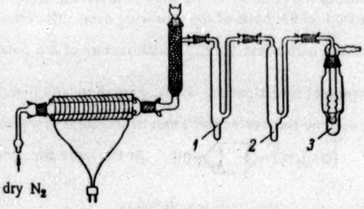


Figure 1. Apparatus for preparation of labeled acetone. 1 and 2) traps for acetone, 3) trap containing 40% KOH solution for absorption of CO_2.

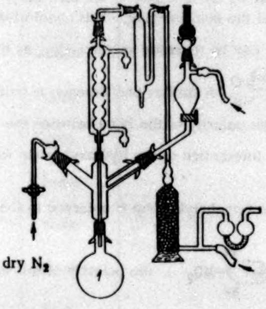


Figure 2. Apparatus for synthesis of labeled tert.-butyl chloride.

Experiments on exchange of labeled tert.-butyl chloride, using the above material, were performed with tert.-butylbenzene and with o-, p- and m-nitro-tert.-butylbenzene.

Results of analysis of a second batch of labeled tert.-butyl chloride, synthesized later, are set forth in Table 3. With this portion, exchange experiments were performed with o-, p- and m-chloro-tert.-butylbenzenes and with o-, p- and m-tert.-butylphenols, as well as experiments on exchange with p-nitro-tert.-butylbenzene in presence of ferric chloride.

TABLE 2

Weight of precipitated $BaCO_3$ (in mg)	Thickness of precipitate (in mg/cm²)	Measured activity* of $BaCO_3$ (in signals per min.)	Activity of uranium standard (0.001 μc) (in signals/min)	Molar activity of $BaCO_3$ (in μc/mole)	Molar activity of tert.-butyl chloride (in μc/mole)
380.0	61.7	447±6	229±3	20.53	82.12
487.5	79.2	429±4	223±1	20.31	81.24
207.3	33.7	407±4	211±3	20.33	81.32
				Mean	81.56

• Measurement of the activity of the sample and of the uranium standard alternated with measurement of the background. The mean for the background is taken from measurements of background before and after measurement of the sample (or standard). The activity of the sample is the mean of five counts (without background). The same applies to the uranium standard. The molar activity of the sample was calculated from the formula of V. G. Vasilyev [5].

TABLE 3

Weight of precipitate of $BaCO_3$ (in mg)	Thickness of precipitate (in mg/cm^2)	Activity of $BaCO_3$ (in signals/min.)	Activity of uranium standard (0.001μc) (in signals/min)	Molar activity of $BaCO_3$ (in μc/mole)	Molar activity of tert.-butyl chloride (in μc/mole)
315.0	51	1508±20	221±6	71.8	287
234.7	38	1647±11	233±2	74.3	297
197.2	32	1509±10	225±3	70.7	283
				Mean	289

For experiments on exchange of tert.-butyl groups between tert.-butylbenzene and its derivatives, tert.-butylbenzene labeled with C^{14} in the tertiary carbon atom of the butyl group was synthesized. Starting substances for the synthesis were benzene and C^{14}-labeled tert.-butyl chloride. The reaction was performed in presence of amalgamated aluminum. Tert.-butylbenzene with a molar activity of 630μc/mole (mean of three analyses) was prepared.

All the remaining substances required for the work were synthesized by us according to the descriptions in the literature.

1. Tert.-butylbenzene was synthesized by two methods: a) using ferric chloride and b) using amalgamated aluminum [6]. The latter method was satisfactory.

2. p- and o-nitro-tert.-butylbenzenes were synthesized by Craig's method [7] (nitration of tert.-butylbenzene). They were separated by numberous fractionations in vacuum. The refractive index served as a criterion of fractionation. p-Nitro-tert.-butylbenzene was purified by freezing out and by recrystallization from gasoline.

3. m-Nitro-tert.-butylbenzene was synthesized by the method of Biekart et al.[1], starting from p-nitro-tert.-butylbenzene.

4. o-, m- and p-chloro derivatives of tert.-butylbenzene were synthesized from the corresponding nitro-tert.-butylbenzenes by conversion to the amino compounds, diazotization, and replacement of the diazo group by chlorine. The products were purified by vacuum distillation and were tested for freedom from nitrogen-containing impurities.

5. o-, m- and p-tert.-butylphenols were obtained from the corresponding diazo compounds by replacement of the diazo group by the hydroxyl group. They were purified by steam distillation followed by distillation in vacuum. p-Tert.-butylphenol was further purified by recrystallization from ligroine.

Constants of our synthesized compounds agreed with the literature data.

The exchange experiments were carried out with equivalent amounts of substances (0.01 mole of each) in sealed glass ampoules. The substance which had been inactive before the experiment was usually analyzed for radioactivity.

Experiments on the exchange of tert.-butyl groups between tert.-butylbenzene and tert.-butyl chloride were performed with labeled tert.-butylbenzene and ordinary tert.-butyl chloride and with unlabeled tert.-butylbenzene (synthesized in presence of ferric chloride) and labeled tert.-butyl chloride. In the first case exchange did not take place except after addition of $AlCl_3$ or $FeCl_3$. In the second case exchange occurs without any addition of catalyst. It is evident that in the case of synthesis of tert.-butylbenzene in presence of ferric chloride, traces of ferric chloride in the active form enter the final product in spite of repeated distillations.

Fractionation of the products after exchange was effected by distillation in a nitrogen stream and redistillation of the fractionated products. Traces of butyl chloride were removed from tert.-butylbenzene by prolonged treatment with concentrated caustic alkali and water. Tert.-butylphenols were dissolved in alkali and the solution freed from traces of volatile substances (tert.-butyl chloride and tert.-butyl alcohol) by passing a stream of

TABLE 4

(Temperature 120°, time 30 hours)

Component mixed with labeled tert.-butylbenzene	Product analyzed	Thickness of precipitate of $BaCO_3$ (in mg/cm^3)	Activity of $BaCO_3$ (in signals/min.)	Activity of standard (in signals/min.)	Molar activity of $BaCO_3$ (in μc/mole)	Molar activity of product (in μc/mole)	Percent of exchange
Tert.-butylbenzene ($FeCl_3$)	Tert.-butylbenzene	51	24 ± 0.6	215 ± 2	1.16	11.6	28.7
		81	24 ± 1	212 ± 2	1.18	11.8	
p-Tert.-butylphenol	p-Tert.-butyphenol	72	46 ± 1	217 ± 6	2.22	22.2	15.4
		121	49 ± 1	229 ± 3	2.25	22.5	
o-Tert.-butylphenol	o-Hydroxy-tert.-butylphenol	39	64 ± 3	223 ± 5	3.03	30.3	21.0
m-Tert.-butylphenol	Tert.-butyl-chloride	16.9	861 ± 10	222 ± 4	41.65	166.6	84.7
	1-Hydroxy-2,5-ditert.-butylbenzene	65	454 ± 5	215 ± 4	22.27	311.8	–

nitrogen while heating on a boiling water bath; the phenols were then separated by the action of sulfuric acid and distilled with steam. After drying, the product was distilled in vacuum. p-Tert.-butylphenol was recrystallized from ligroine. Its purity was checked by the melting point.

As was indicated above, a substitution product was the main product isolated after exchange with m-tert.-butylphenol. A molecular weight determination showed that this substance is a monomer in 1:2,500 solution in benzene, and is di-tert.-butylphenol (found M 222; calc. 206). In camphor at 1:11 concentration it is a dimer (found M 424; calc. 412). The melting point of this product is 121-122°. It is evidently 2,5-ditert.-butylphenol.

Results of exchange experiments are presented in Table 4.

The molar activity of the original labeled tert.-butyl chloride was 81.56 μc/mole in the case of exchange with tert.-butylbenzene and 289 μc/mole in the cases of exchange with hydroxy derivatives of tert.-butylbenzene.

As already indicated, the main product isolated after the experiment with m-tert.-butylphenol was 2,5-ditert.-butylphenol. Its activity at the given degree of exchange and at the equilibrium established should be 289 μc/mole; we found a value of 311.8 μc/mole, i. e., 7.9% different from the theoretical. This difference may have been due to equilibrium not yet attained.

Experiments on exchange of tert.-butyl groups between tert.-butyl chloride and o-, m- and p-derivatives of tert.-butylbenzene at 120° for 20 hours showed that no exchange occurs under these conditions. Addition of ferric chloride to the system p-nitro-tert.-butylphenol + tert.-butyl chloride did not lead to exchange. Irradiation with the quartz lamp likewise had no effect.

Experiments were also performed on the exchange of tert.-butyl groups between C^{14}-labeled tert.-butylbenzene and its derivatives. Results are presented in Table 5.

The data of Table 5 show that there is no exchange of groups between tert.-butylbenzene and its derivatives. Traces of exchange were only detected with the hydroxyl derivative in presence of catalyst.

SUMMARY

1. An investigation was made of exchange of tert.-butyl groups between tert.-butylbenzene and its nitro-, chloro- and hydroxy- derivatives on the one hand with tert.-butyl chloride labeled with C^{14} in the tertiary carbon atom on the other hand. It was found that exchange in the absence of a catalyst only takes place in the case of hydroxy- derivatives. Introductionof the nitro group and chlorine into the benzene ring inhibits the exchange reactions.

TABLE 5

(Temperature 120°)

Component mixed with labeled tert.-butylbenzene	Duration (hours)	Activity of product (in signals/min.)
p-Amino-tert.-butylbenzene	20	None
p-Tert.-butylphenol + dioxane* + $FeCl_3$	30	6.4**
p-Nitro-tert.-butylbenzene* + dioxane + $FeCl_3$	30	None

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* Analogous results were obtained in presence of $AlCl_3$. Rise of temperature to 220° leads to severe resinification.

** Amount of product used in testing for activity was 0.06 g.

2. Exchange takes place with the greatest facility in the case of m-tert.-butylphenol, followed (in decreasing order) by o-tert.-butylphenol and p-tert.-butylphenol.

3. Very slight exchange of groups between labeled tert.-butylbenzene and p-tert.-butylphenol was observed in the presence of a catalyst ($FeCl_3$, $AlCl_3$).

4. The hypothesis is advanced that exchange proceeds by an ionic mechanism and that in the case of such a mechanism of exchange the mobility of a group or atom influences the polarity of the bond between the given group (or atom) and the carbon in the aromatic ring.

LITERATURE CITED

[1] H. J. B. Biekart, H. B. Dessens, P. E. Verkade and B. M. Wepster, Rec. trav. chim. 71, 325 (1952).

[2] E. L. Illingworth and A. T. Peters, J. Chem. Soc. 1952, 2730.

[3] G. A. Ropp, O. Kenton and Neville, Nucleonics 9, 22 (1951).

[4] I. P. Gragerov, Proc. Acad. Sci. USSR 99, 101 (1954).

[5] V. G. Vasilyev, J. Anal. Chem. 10, 368 (1955) (T.p. 359).*

[6] L. J. Diuguid, J. Am. Chem. Soc. 63, 3527 (1941).

[7] D. Craig, J. Am. Chem. Soc. 57, 195 (1935).

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* T.p. = C. B. Translation pagination.

TABLE 5

(Temperature [illegible])

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4. The [illegible]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

Additional results were obtained in presence of [illegible]

LITERATURE CITED

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[4] J. R. [illegible], Proc. Amer. Soc. [illegible]

[illegible]

SUMMARY

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THE CATALYZED VAPOR-PHASE HYDROLYSIS OF HALO DERIVATIVES OF ORGANIC COMPOUNDS

I. HYDROLYSIS OF 1,2,4-TRICHLOROBENZENE

A. I. Naumov and Z. G. Lapteva

The catalytic vapor-phase hydrolysis of dichlorobenzenes is known to go with considerably greater difficulty than the hydrolysis of chlorobenzene [1]. On the other hand, it has been noted that the mobility of the halogen increases with increasing number of chlorine atoms in the benzene ring in the liquid-phase alkaline hydrolysis [2].

Interest is attached to a study of the mobility of the halogen when several halogen atoms are present in a benzene ring during vapor-phase hydrolysis. There are no literature data on this problem with the exception of one patent [3].

In the present paper we submit the results of a study of the vapor-phase hydrolysis of 1,2,4-trichlorobenzene in presence of a phosphate catalyst. Clorine is replaced by hydrogen to a greater or lesser extent in the vapor-phase hydrolysis of chlorobenzene and dichlorobenzene; the hydrogen is mainly formed by oxidation [4]. It was to be expected that these reactions would also take place during hydrolysis of trichlorobenzene.

More than 20 products could result from the hydrolysis of $C_6H_3Cl_3$ if we allow for all possible degrees of substitution of chlorine by hydroxyl and hydrogen.

With such an abundance of possible products, the determination of the composition of a catalyzate presents great difficulties, particularly since many of the compounds have very similar physical constants and are lacking in specific reactions for their identification.

The study of the reaction over a phosphate catalyst revealed that substantially only one product was formed – m-chlorophenol. We found this result not unexpected. It must be remembered that the liquid-phase hydrolysis of 1,2,4-trichlorobenzene with sodium ethoxide in methanol at 180° gives 2,5-dichlorophenol [5].

It was found that the main factor governing the selectivity of this catalyst in respect of the formation of m-chlorophenol (and of phenols in general) is the temperature.

The dependence of the yield (β) of m-chlorophenol on the temperature is plotted in Fig. 1. The yield is defined as the ratio of the amount of HCl corresponding to the formation of m-chlorophenol to the total amount of HCl formed: $\beta = \frac{2n_1C_6H_4ClOH}{n_2HCl}$, where n_1 and n_2 are respectively the number of moles of m-chlorophenol and HCl.

As we see from Fig. 1, the selectivity of formation of m-chlorophenol falls linearly with rising temperature when the experimental conditions are varied over wide limits. Apart from the temperature, an appreciable influence upon the selectivity of the action of the catalyst is exerted by the duration of contact and by the concentration of trichlorobenzene.

The yield of m-chlorophenol is plotted as a function of duration of contact in Fig. 2, and as a function of concentration of trichlorobenzene in Fig. 3.

Figure 2 shows that in all cases the yield of m-chlorophenol falls with increasing duration of contact. Figure 3 shows that the yield increases with rising concentration of trichlorobenzene. It should be noted that we succeeded

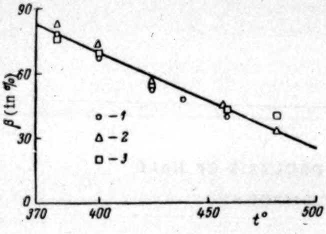


Figure 1. Yield of m-chlorophenol as a function of temperature.
1) $C_{TCB} = 0.135$ and $\tau = 0.85$ sec, 2) $C_{TCB} = 0.299$ and $\tau = 1.24$, 3) $C_{TCB} = 0.467$ and $\tau = 1.52$.

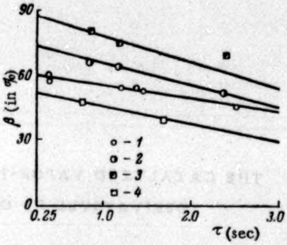


Figure 2. Yield of m-chlorophenol as a function of duration of contact.
1) $C_{TCB} = 0.290$, 425°, 2) $C_{TCB} = 0.145$, 400°, 3) $C_{TCB} = 0.145$, 380°, 4) $C_{TCB} = 0.516$, 460°.

for the first time in observing a rise in the yield of phenol (reckoned on the reacted trichlorobenzene) with increasing concentration of chloro derivative when the concentration of water in the vapor-phase hydrolysis of aryl halides was reduced.

All investigators of the vapor-phase hydrolysis of halo derivatives of hydrocarbons mention the necessity of using a large excess of water in order to prevent pyrolysis [6].

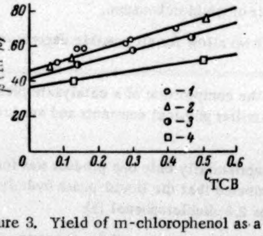
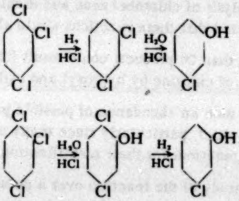


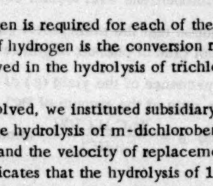
Figure 3. Yield of m-chlorophenol as a function of the original concentration of trichlorobenzene.
1) 425°, $\tau = 0.43$ sec; 2) 425°, $\tau = 0.89$ sec; 3) 400°, $\tau = 2.44$ sec; 4) 460°, $\tau = 0.86$ sec.

Stabilized formation of m-chlorophenol under various conditions may be realized by two routes:

1)



2)



Hydrogen is required for each of these schemes. A rich source of hydrogen is the conversion reaction that we always observed in the hydrolysis of trichlorobenzene.

In order to establish which of the above schemes is actually involved, we instituted subsidiary experiments whose objectives were the determination of the velocity of vapor-phase hydrolysis of m-dichlorobenzene, the velocity of replacement of chlorine by hydrogen in trichlorobenzene, and the velocity of replacement of chlorine by hydrogen in 2,5-dichlorophenol. An examination of the results indicates that the hydrolysis of 1,2,4-trichlorobenzene proceeds mainly according to the second scheme via formation of 2,5-dichlorophenol. Consequently, the kinetics of formation of m-chlorophenol reflect the kinetics of formation of 2,5-dichlorophenol. Hardly any replacement of chlorine is observed when molecular hydrogen acts on trichlorobenzene, but hydrogen formed during the reaction replaces chlorine.

It was of interest to determine the kinetic form of the reaction of hydrolysis of trichlorobenzene. It was found that in a wide range of change of concentration of the original trichlorobenzene, the reaction is expressed by the equation:

$$\frac{-dC_{TCB}}{d\tau} = K\sqrt{C_{TCB}} \quad (1)$$

where C_{TCB} is the molar concentration of trichlorobenzene.

Substituting the existing concentration for the original, and integrating equation (1), we have

$$K = \frac{2\sqrt{C^0_{TCB}}}{\tau}(1 - \sqrt{1-\alpha}), \quad (2)$$

where α is the degree of transformation of trichlorobenzene, and τ is the period of contact.

Results obtained by varying and C^0_{TCB} are presented in the table [the velocity constant K is calculated from equation (2)].

Dependence of Degree of Transformation of Trichlorobenzene into m-Chlorophenol on the Concentration of Trichlorobenzene

C_{TCB} (in moles)	Period of contact τ (in sec.)			
	0.89		1.29	
	α (%)	$K \cdot 10^2$	α (%)	$K \cdot 10^2$
0.004	26	1.80*	—	—
0.0164	15.7	2.04**	—	—
0.050	8.4	2.15	9.5	1.70
0.150	4.7	2.07	6.5	1.98
0.300	3.4	2.10	4.5	1.93
0.500	2.5	2.0	—	—

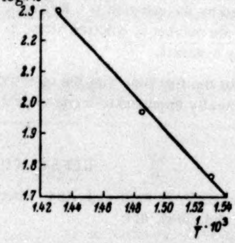


Figure 4. Velocity constant of the formation of m-chlorophenol as a function of temperature.

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* τ = 1.0 sec.

** τ = 1.04 sec.

In addition to m-chlorophenol, the catalyzate contains small amounts of other phenols (resorcinol and hydroquinone) in a total of not more than 2-10% of the m-chlorophenol. In the determination of α, these impurities were assumed to be m-chlorophenol.

As we see from the table, the constancy of the velocity constant is satisfactory within the limits of experimental error. The velocity constant varies more when τ is varied.

The velocity constant is plotted against temperature in Fig. 4. The points lie satisfactorily on a straight line in conformity with the Arrhenius law. The slope of this straight line gives a value of the apparent energy of activation of 25,020 cal/mole.

EXPERIMENTAL

Experiments were carried out in a quartz tube which was inserted in an electrically heated tube furnace. The temperature in the catalyst was kept constant to within ± 1.5° (the reaction has almost no thermal effect). A constant feed of reactants was maintained automatically to within ± 2%. The trichlorobenzene was previously purified by numerous distillations in an efficient column, and had b. p. 213°, m. p. 16.8°, n_D^{20} 1.5718.

Method of analysis of catalyzate. The catalyzate comprised two layers in which brominatable products were present. The layers were separated. The organic layer was treated with small portions of water for extraction of diphenols. After extraction, the solution was combined with the aqueous layer, which was then analyzed for its content of hydrogen chloride and total content of brominatable compounds by Koppeschaar's method [7]. The aqueous solution was then repeatedly treated with ether for extraction of the phenols. The ether was driven off from the ethereal solution and the concentrate was qualitatively analyzed for hydroquinone and diphenols. In all cases insignificant amounts of resorcinol, very little hydroquinone and substantially no pyrocatechol were detected. The total content of brominatables was determined in the organic layer. Thereupon the ethereal extract from the water layer was combined with the organic layer and the total solution was treated with alkali for extraction of the monophenols and their examination. For the latter purpose, the phenols were converted into phenoxy derivatives and benzoates [8]. The phenoxy derivative of the main product of the catalysis had usually m. p. 107.6-108°; its benzoate had m. p. 67.6-67.8°. According to the literature the phenoxy derivative of m-chlorophenol melts at 109° and its benzoate at 71°. No melting point depression was observed in a mixed test of the benzoates.

In five passes the degree of transformation of the trichlorobenzene into m-chlorophenol reached 32%. Phenol was detected in the final products of reaction, in addition to dichlorobenzenes.

SUMMARY

The process of vapor-phase hydrolysis of 1,2,4-trichlorobenzene in presence of phosphate catalyst is accompanied by the replacement of one atom of chlorine by hydrogen with the result that the main reaction product is m-chlorophenol. The speed of formation of m-chlorophenol is governed by the speed of formation of 2,5-dichlorobenzene and is expressed by the equation $w = K\sqrt{C_{TCB}}$. The apparent energy of activation was found to be 25,020 cal/mole. Increase of the number of chlorine atoms to three does not significantly alter their mobility in the reaction of substitution by hydroxyl.

It was observed for the first time that the selectivity of the action of the catalyst in vapor-phase hydrolysis is not lowered but is actually improved to a considerable extent by a sharp drop in the concentration of water vapor.

LITERATURE CITED

[1] M. A. Popov and V. A. Popova, J. Appl. Chem. 9, 1303 (1936); L. Freidlin and G. Fridman, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1949, 317.

[2] N. N. Vorozhtsov, Fundamentals of Synthesis of Intermediates and Dyes (1950), 405.

[3] U. S. Patent 1849844; Chem. Zentr. 1932, 1, 2994.

[4] N. N. Vorozhtsov, Fundamentals of Synthesis of Intermediate Products and Dyes (1950), 402, 423 and 424; L. Freidlin et al., Bull. Acad. Sci. USSR, Div. Chem. Sci. 1946, 439.

[5] R. Hollemann, Rec. trav. chim. 37, 201 (1918).

[6] L. Kh. Freidlin, Progr. Chem. 23, 581 (1954).

[7] Koppeschaar, Z. anal. Chem. 15, 232 (1876).

[8] Johnson, Shannon and Reed, Organic Reagents for Organic Analysis (1948), 46, 49.

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State Institute of Research on Organic
Intermediates and Dyes

SYNTHESIS OF CHLORO- AND BROMO-SUBSTITUTED METHYLSTYRENES

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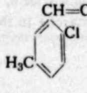
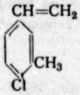
Substituted styrenes attract the attention of investigators because they facilitate study of the influence of the character of the substituted groups on the susceptibility to polymerization and on the properties of the polymers obtained. In addition, substituted styrenes find varied practical applications. Styrene derivatives substituted in the ring with methyl groups [1] or halogen atoms [2] have long been known, but derivatives containing both halogen atoms and a methyl group in the benzene ring have not been described. We have therefore synthesized: 2-chloro-5-methylstyrene (I), 4-chloro-3-methylstyrene (II), 2-bromo-5-methylstyrene (III) and 4-bromo-3-methylstyrene (IV).



(I)



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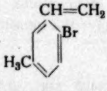
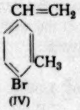
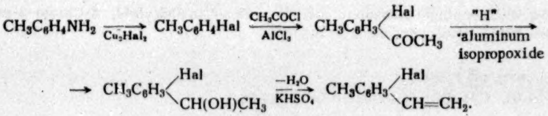


(III)



(IV)

The synthesis of halogen-substituted methylstyrenes may be represented by the following scheme:



$$CH_3C_6H_4NH_2 \xrightarrow[Cu_2Hal_2]{} CH_3C_6H_4Hal \xrightarrow[AlCl_3]{CH_3COCl} CH_3C_6H_3\begin{cases}Hal\\ COCH_3\end{cases} \xrightarrow[\text{aluminum isopropoxide}]{\text{"H"}}$$

$$\rightarrow CH_3C_6H_3\begin{cases}Hal\\ CH(OH)CH_3\end{cases} \xrightarrow[KHSO_4]{-H_2O} CH_3C_6H_3\begin{cases}Hal\\ CH{=}CH_2.\end{cases}$$

EXPERIMENTAL

Synthesis of 2-chloro-5-methylstyrene. The starting substance was p-toluidine which was diazotized to give p-chlorotoluene with b. p. 161-162°, n_D^{24} 1.5194 (the literature gives n_D^{24} 1.5193). Yield 65-70%.

Preparation of 2-chloro-5-methylacetophenone. 126.5 g (1 mole) p-chlorotoluene and 154 g (1 mole) pulverized anhydrous aluminum chloride were placed in a three-necked flask fitted with reflux condenser, mechanical stirrer and dropping funnel. Dropwise addition, with cooling, was made of 90 g (1 mole) acetyl chloride. At the conclusion of the reaction, the mixture was heated on a water bath for 1 hour, and after cooling it was run into a large volume of water acidified with HCl. The liquid was extracted with ether and the ethereal solution was washed with 5% caustic alkali solution and then with water, and dried with calcium chloride. After removal of ether, the residue was distilled in vacuum. Yield 70%. A colorless transparent liquid with b. p. 80-83° (2 mm), n_D^{20} 1.5430.

Preparation of 2-chloro-5-methylphenyl-methylcarbinol. 85.3 g (0.5 mole) 2-chloro-5-methylacetophenone was dissolved in 500 ml anhydrous isopropyl alcohol in a round-bottomed flask to which was attached a column and a condenser; a solution of aluminum alcoholate (prepared from 15 g aluminum) was added and the mixture heated on a water bath in such a way that not more than 3-5 drops distillate came over per minute. After 3-4 hours the rate of distillation was increased and a large proportion of the isopropyl alcohol and acetone formed was distilled off. The whole process of reduction required 6 hours. The residue in the flask was cooled, treated with 10% HCl and extracted several times with benzene. The benzene solution was dried over anhydrous sodium sulfate, the benzene was driven off and the residue was distilled in vacuum. Yield 65%. A colorless, transparent liquid.

B. p. 82° (1 mm), n_D^{19} 1.5392.
Found %: Cl 21.15. $C_9H_{11}OCl$. Calculated %: Cl 20.82.

Preparation of 2-chloro-5-methylstyrene. 30 g of the carbinol and 6 g freshly ignited potassium bisulfate were placed in a flask fitted with a column and a condenser. In presence of a polymerization inhibitor the mixture was cautiously heated at 50-60° and 90-100 mm; monomer and water distilled over. The monomer was dissolved in ether and the solution washed with caustic alkali, water, saturated calcium chloride solution and again with water; it was dried over anhydrous calcium chloride. The ether was driven off and the residue distilled in vacuum. After 2-3 distillations the monomer was obtained in the form of a colorless, transparent liquid with the odor of styrene. Yield 25%.

B. p. 52° (1 mm), n_D^{20} 1.5601, d_4^{20} 1.074, MR_D 45.96; calc. 45.88.
Found %: Cl 23.60. C_9H_9Cl. Calculated %: Cl 23.28.

Synthesis of 2-bromo-5-methylstyrene. The starting substance was p-bromotoluene with m. p. 27-28°. Acetylation of p-bromotoluene (like the synthesis of the chloro derivative) gave 2-bromo-5-methylacetophenone in 50% yield in the form of a colorless, transparent liquid with b. p. 101-102° (2 mm), n_D^{18} 1.5815. Reduction of 2-bromo-5-methylacetophenone gave the carbinol in 45% yield. A colorless transparent liquid with b. p. 112-115° (1-2 mm), n_D^{20} 1.5672. Dehydration of the carbinol gave the monomer of 2-bromo-5-methylstyrene in the form of a colorless liquid with an odor of styrene.

B. p. 59° (1 mm), n_D^{20} 1.5872, d_4^{20} 1.3480, MR_D 49.15; calc. 48.78.
Found %: Br 41.05. C_9H_9Br. Calculated %: Br 40.61.

Synthesis of 4-chloro-3-methylstyrene. Diazotization of o-toluidine gave o-chlorotoluene with b. p. 156-158°, n_D^{20} 1.5240 (the literature reports n_D^{20} 1.5241) in 64% yield. Acetylation of o-chlorotoluene gave 4-chloro-3-methylacetophenone with b. p. 120° (7 mm), 265-270° (760 mm) (the literature reports 262-269°), n_D^{20} 1.5495. Yield 67%. Reduction with aluminum alcoholate gave the carbinol in 65% yield. 4-Chloro-3-methylphenylmethylcarbinol is a colorless liquid, rapidly darkening in the light.

B. p. 118° (4-5 mm), n_D^{25} 1.5390.
Found %: Cl 20.89. $C_9H_{11}OCl$. Calculated %: Cl 20.88.

Dehydration of the carbinol over potassium bisulfate gave 4-chloro-3-methylstyrene in the form of a colorless, transparent liquid with the odor of styrene. Yield 26%.

B. p. 53° (1 mm), n_D^{20} 1.5600, d_4^{20} 1.074, MR_D 45.78; calc. 45.88.
Found %: Cl 22.57. C_9H_9Cl. Calculated %: Cl 23.28.

Synthesis of 4-bromo-3-methylstyrene. Diazotization of o-toluidine gave o-bromotoluene in the form of a transparent, slightly yellowish liquid, b. p. 181-182°, n_D^{20} 1.5606 (the literature gives 1.5608). Yield 54%. Acetylation of o-bromotoluene gave 4-bromo-3-methylacetophenone in the form of a transparent, yellowish liquid with b. p. 97-100° (2-3 mm), n_D^{20} 1.5765. Yield 63%. It was reduced to the carbinol, a transparent, yellowish liquid which darkens in the air. 4-Bromo-3-methylphenylmethylcarbinol has b. p. 140° (3-5 mm), n_D^{20} 1.5670.

Found %: Br 37.48. $C_9H_{11}OBr$. Calculated %: Br 37.21.

Dehydration of the carbinol and two distillations gave 4-bromo-3-methylstyrene. Colorless, transparent liquid with the odor of styrene. Yield 22%.

B. p. 61° (1 mm), n_D^{20} 1.5885, d_4^{20} 1.3640, MR_D 48.23; calc. 48.47.
Found %: Br 40.54. C_9H_9Br. Calculated %: Br 40.61.

SUMMARY

The previously undescribed 2-chloro(bromo)-5-methylstyrenes and 4-chloro(bromo)-3-methylstyrenes were synthesized and characterized.

LITERATURE CITED

[1] P. P. Shorygin and N. V. Shorygina, J. Gen. Chem. 5, 555 (1935); J. Dixon, K. Saunders, Ind. Eng. Chem. 46, 652 (1944).

[2] P. P. Shorygin and N. V. Shorygina, J. Gen. Chem. 9, 845 (1939); S. N. Ushakov and P. Matuzov, J. Gen. Chem. 14, 120 (1944); L. Brooks, J. Am. Chem. Soc. 66, 29 (1943); E. Matsui, C. A. 44, 9186 (1950); M. M. Koton et al., J. Gen. Chem. 21, 1843 (1951) (T.p. 2043) •; M. M. Koton and E. M. Moskvina, J. Appl. Chem. 26, 660 (1953) (T.p. 617). •

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• T.p. = C. B. Translation pagination.

THE CONDENSATION OF STYRENE WITH BENZENE

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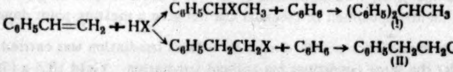
In connection with a study of the possibilities of radical reactions during alkylation of the aromatic ring, we have again carried out an investigation of the condensation of styrene with benzene; in doing so, we had in mind the probability of intermediate addition of hydrogen halides [1] which takes place under certain conditions as a radical reaction; the formation of either 1,1-diphenylethane (I) or dibenzyl (II) is therefore possible:



$$C_6H_5CH{=}CH_2 + HX \begin{array}{l} \nearrow C_6H_5CHXCH_3 + C_6H_6 \rightarrow \underset{(I)}{(C_6H_5)_2CHCH_3} \\ \searrow C_6H_5CH_2CH_2X + C_6H_6 \rightarrow \underset{(II)}{C_6H_5CH_2CH_2C_6H_5} \end{array}$$

Schramm [2] had already obtained 1,1-diphenylethane from styrene and benzene in presence of $AlCl_3$. Nenitzescu [3] repeated this reaction and isolated only a very small amount (5%) of 1,1-diphenylethane due to the simultaneous polymerization of the styrene. Up to 60% 1,1-phenylarylethanes is obtained from benzene and its homologs with styrene in presence of sulfuric acid [4, 5].

In our laboratory, in the course of study of the condensations of acetylene with benzene in presence of $AlCl_3$, we also carried out reactions with styrene and obtained up to 40% 1,1-diphenylethane [6].

We studied these reactions in an endeavor to establish the conditions under which polymerization would not occur. It was found necessary to use a very large excess of benzene, a minimum amount of $AlCl_3$, and low temperatures. Careful addition of 0.1 mole styrene to a mixture of 6 moles benzene and 0.01 mole $AlCl_3$ at 40° gives 50-60% 1,1-diphenylethane. Gradual addition of a hydrogen halide (HCl or HBr) to the reaction mixture slightly improves the yield of 1,1-diphenylethane. If, however, the styrene is added to the benzene which had previously been saturated with HCl or HBr, then the styrene rapidly polymerizes.

Kharasch has studied the anomalous additions of hydrogen halides to olefins. It was shown [7] that such additions go readily with HBr in presence of peroxy compounds and solvents. A high yield of β-bromoethylbenzene was obtained from styrene. With HCl Kharasch always obtained α-chloroethylbenzene. The possibility, however, of radical addition of HCl to the double bond was also shown recently [8].

Kharasch observed that metallic halides decompose the peroxy compounds and the anomalous addition does not then take place [9]. This is consistent with the failure to detect an influence of benzoyl peroxide upon the condensation of chloroolefins with benzene in presence of $AlCl_3$ [10].

We studied the addition of HBr to styrene under the influence of light (PRK-2 lamp) in presence of $AlBr_3$ and $AlCl_3$ in the expectation that the anomalous course of the reaction might then persist.

Actually, under these conditions, which hindered facile polymerization of styrene, we obtained β-bromoethylbenzene (73%). The reaction was conducted in solutions in benzene and ligroine containing small amounts of $AlBr_3$ at 10-15°. Styrene was added in small portions at the same time as the HBr was introduced. In order to exclude the influence of peroxides, which rapidly accumulate when styrene is stored, the latter was distilled before the experiment, and diphenylamine was added. Control experiments in the absence of irradiation gave only α-bromoethylbenzene. The same product was also obtained in the absence of solvents during irradiation. The possibility was accordingly established of carrying out radical alkylation reactions with styrene. Such an alkylation could not be effected in one stage since all amounts of $AlCl_3$ were used in order to avoid polymerization. The separated β-bromoethylbenzene was easily indentified, however, by condensing it with benzene to form dibenzyl in nearly quantitative yield.

EXPERIMENTAL

Condensation of styrene with benzene. In the course of 2 hours 10 g styrene in 150 ml benzene was added in small portions to a suspension of 1 g $AlCl_3$ in 400 ml benzene. The reaction was performed with stirring and heating to 40°. The mixture was then run into water, and the benzene layer was separated, washed and dried. Fractionation of the crude product gave 9 g (50%) 1,1-diphenylethane, with b. p. 268-270°, n_D^{20} 1.5760, d_4^{20} 1.0030. Oxidation with chromic oxide in acetic acid [11] gave benzophenone with m. p. 48°; oxime m. p. 143°.

Addition of HBr to styrene under the influence of light in presence of $AlBr_3$. 450 ml benzene and 2.5 g $AlBr_3$ were put into a quartz flask provided with a stirrer, a dropping funnel and tubes for supplying and discharging HBr. A stream of dry HBr was introduced while irradiating with a PRK-2 lamp. At the same time a solution of 10 g freshly distilled styrene and 0.34 g diphenylamine in 150 ml benzene was added dropwise. The reaction lasted 2 hours, and the temperature of the mixture was kept at 12-15°.

Processing in the usual manner gave 13 g (73%) β-bromoethylbenzene with b. p. 100-102° (at 17 mm); n_D^{20} 1.5533, d_4^{20} 1.3032.

Condensation of β-bromoethylbenzene with benzene. 12.4 g product from the preceding reaction, 25 ml benzene and 2.5 g $AlBr_3$ were heated on a water bath at 40-50° for 3 hours to give 12 g (97%) dibenzyl with m. p. 51°. A mixed test with an authentic specimen of dibenzyl did not give a melting point depression.

A control experiment on the addition of HBr to styrene without irradiation was carried out with the same amounts of reactants and under the same conditions, but without irradiation. Yield 13.5 g (76%) α-bromoethylbenzene with b. p. 113-114° (at 35 mm), n_D^{20} 1.5460, d_4^{20} 1.3470. Condensation of 10 g of the product with benzene (25 ml) gave 6.9 g (53%) of 1,1-diphenylethane with b. p. 148-150° at 20 mm, n_D^{20} 1.5760, d_4^{20} 1.0030. Oxidation yielded benzophenone with m. p. 48°; oxime m. p. 143°.

SUMMARY

1. Condensation of styrene with benzene can be effected in very dilute benzene solutions at low temperatures and with the help of small amounts of aluminum salts; yields of 1,1-diphenylethane reach 50-60%.

2. The possibility is demonstrated of radical addition of hydrogen bromide to styrene under the influence of light. Aluminum halide does not interfere with this reaction. β-Bromoethylbenzene is obtained in 73% yield.

3. Condensation of styrene with benzene under irradiation and in presence of hydrogen bromide leads, via intermediate formation of β-bromoethylbenzene, to dibenzyl. Total yield of dibenzyl 70.8%.

LITERATURE CITED

[1] N. N. Lebedev, J. Gen. Chem. 24, 1782 (1954) (T.p. 1751).*

[2] J. Schramm, Ber. 26, 1706 (1893).

[3] C. Nenitzescu, D. Jsacescu and C. Jonescu, Ann. Chem., Justus Liebigs 491, 219 (1931).

[4] G. Kraemer and A. Spilker, Ber. 23, 3169 (1890); 24, 2785 (1891).

[5] A. Spilker, W. Schade, Ber. 65, 1686 (1932).

[6] I. P. Tsukervanik, Bull. Acad. Sci. Uk. SSR 1946, No. 11, 3.

[7] C. Walling, S. Kharasch and R. Mayo, J. Am. Chem. Soc. 61, 2693 (1939).

[8] B. Frank and R. Mayo, J. Am. Chem. Soc. 76, 5392 (1954).

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* T.p. = C. B. Translation pagination.

[9] S. Kharasch and W. Hannum, J. Am. Chem. Soc. 56, 712 (1934).

[10] J. Colonge and P. Garnier, Bull. soc. chim. 1948, 436.

[11] Dict. Org. Compounds (1949), I, 1027.

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Sciences of the Uzbek SSR

[7] S. Kharasch and W. [illegible], J. Am. Chem. Soc. [illegible] (194[illegible])

[8] J. Colonge and [illegible], Bull. soc. chim., 1950, [illegible]

[9] Dict. Org. Compounds (1946) 1, [illegible]

CONDENSATION OF DIMETHYLANILINE WITH ACETYLENE AND ACETALDEHYDE

T. G. Garkovets and I. P. Tsukervanik

The alkylation of the aromatic nucleus with acetylene has been studied previously [1]. These reactions go according to the scheme

$$ArH + C_2H_2 \xrightarrow[AlCl]{} ArCH{=}CH_2 \xrightarrow[AlCl_3]{ArH} (Ar)_2CHCH_3,$$

so that with dimethylaniline we can obtain p-dimethylaminostyrene (I) and 1,1-di-(4-dimethylaminophenyl)-ethane (II):

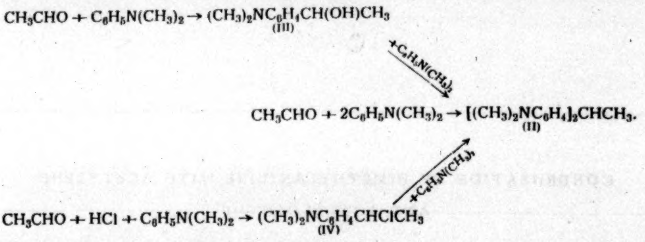
$$(CH_3)_2NC_6H_5 + C_2H_2 \xrightarrow[AlCl_3]{} (CH_3)_2NC_6H_4CH{=}CH_2 \xrightarrow[AlCl_3]{+C_6H_5N(CH_3)_2} [(CH_3)_2NC_6H_4]_2CHCH_3.$$

Cook and Chambers [2] studied reactions of acetylene with aromatic compounds and carried out the condensation with dimethylaniline. They obtained traces of a substance which, on the basis of some qualitative tests, was assumed to be (II). Since in reactions of anilines with acetaldehyde the products obtained are frequently the same as when using acetylene [3], we studied at the same time the condensations of dimethylaniline with both substances.

Trillat [4] unsuccessfully attempted to react acetaldehyde with dimethylaniline in presence of H_2SO_4. He obtained substance (II) only in minute yield when using a mixture of the products of oxidation of ethyl alcohol in place of acetaldehyde. He interpreted the reaction as a condensation of ethyl acetal with dimethylaniline.

We studied the condensations of acetylene and acetaldehyde with dimethylaniline under a wide range of experimental conditions. Variations were made in the temperature, ratio of reactants, catalysts and their amount, and the duration of the reaction. In the experiments with acetylene we established that when using 0.023-1.5 moles $AlCl_3$ per mole of dimethylaniline, the reaction goes at a temperature not lower than 60° with formation of (II). The best yield (30% on the dimethylaniline entering into reaction, was obtained [5] by introducing 0.5 mole $AlCl_3$ into the dimethylaniline heated to 100°, and passing a stream of acetylene while stirring mechanically. This dependence of the reaction on the temperature is evidently governed by the character of the complexes of the reactants with $AlCl_3$. The yield of (II) was later raised to 43% by carrying out the reaction with excess of dimethylaniline. Utilization of samples of $AlCl_3$ diluted in various ways did not give good results. The p-dimethylaminostyrene (I) expected according to the scheme was not detected among the reaction products.

Condensation with acetaldehyde in presence of acid catalysts could possibly go according to three mechanisms, all ultimately leading to (II):



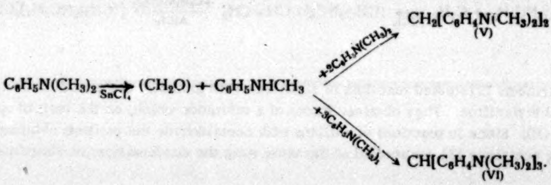
$$CH_3CHO + C_6H_5N(CH_3)_2 \rightarrow \underset{(III)}{(CH_3)_2NC_6H_4CH(OH)CH_3} \xrightarrow{+C_6H_5N(CH_3)_2}$$

$$CH_3CHO + 2C_6H_5N(CH_3)_2 \rightarrow \underset{(II)}{[(CH_3)_2NC_6H_4]_2CHCH_3}.$$

$$CH_3CHO + HCl + C_6H_5N(CH_3)_2 \rightarrow \underset{(IV)}{(CH_3)_2NC_6H_4CHClCH_3} \xrightarrow{+C_6H_5N(CH_3)_2}$$

Experiments with acetaldehyde and paraldehyde under the conditions of these schemes led to formation of (II) in a yield of up to 44% when using $AlCl_3$ and H_2SO_4 as catalysts (III) and (IV) were not detected among the reaction products; we therefore concluded that the condensation of acetaldehyde with dimethylaniline goes as a dehydration reaction. We followed this up by experiments using various dehydrating agents (anhydrous oxalic acid, chlorosulfonic acid, phosphorus trichloride, phosphorus oxychloride, and potassium bisulfate). In all cases (II) was isolated. Its best yield (70%) was obtained when using chlorosulfonic acid.

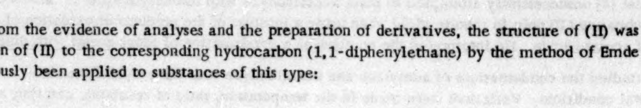
When using other catalysts ($SnCl_4$, $FeCl_3$, $HgCl_2$, $CuCl_2$) in condensations of acetylene and acetaldehyde with dimethylaniline, and also in experiments with $AlCl_3$ in nitrobenzene solution, the expected (II) was not obtained, its place being taken by di-(4-dimethylaminophenyl)-methane (V) and tri-(4-dimethyl-aminophenyl)-methane (VI) (leuco bases of crystal violet). Formation of these substances is evidently the result of oxidative cleavage and autocondensation of dimethylaniline, proceeding when the normal reaction is inhibited:



$$C_6H_5N(CH_3)_2 \xrightarrow[SnCl_4]{} (CH_2O) + C_6H_5NHCH_3 \xrightarrow{+2C_6H_5N(CH_3)_2} \underset{(V)}{CH_2[C_6H_4N(CH_3)_2]_2}$$

$$C_6H_5N(CH_3)_2 \xrightarrow[SnCl_4]{} (CH_2O) + C_6H_5NHCH_3 \xrightarrow{+3C_6H_5N(CH_3)_2} \underset{(VI)}{CH[C_6H_4N(CH_3)_2]_3}.$$

Apart from the evidence of analyses and the preparation of derivatives, the structure of (II) was confirmed by deamination of (II) to the corresponding hydrocarbon (1,1-diphenylethane) by the method of Emde [6] which had not previously been applied to substances of this type:



$$[(CH_3)_2NC_6H_4]_2CHCH_3 + CH_3I \rightarrow [(CH_3)_3\underset{I}{N}C_6H_4]_2CHCH_3 \xrightarrow{H_2} (C_6H_5)_2CHCH_3 + (CH_3)_3N.$$

EXPERIMENTAL

Condensation of acetylene with dimethylaniline in presence of $AlCl_3$. 63 ml dimethylaniline was placed in a three-necked flask fitted with mechanical stirrer and tubes for introduction and discharge of gases. Acetylene was passed at a speed of 15 liters per hour from a gas tank into dimethylaniline heated on a boiling water bath; at the same time 33 g finely pulverized $AlCl_3$ was added in small portions over a period of $1\frac{1}{2}$ hours; the mixture was mechanically stirred. Duration of reaction 4 hours. Acetylene not entering into reaction was collected in a second gas tank. The cooled reaction mixture was treated with iced water and then made alkaline until an oily layer was formed; the latter was collected and distilled with steam. The distillate (45 ml) was unreacted dimethylaniline. The residue (9.9 g) was extracted with ligroine. Fractionation gave 6.5 g (34.2%) 1,1-di-(4-dimethylaminophenyl)-ethane (II).

In another experiment 250 ml dimethylaniline, 100 liters acetylene, and 33 g $AlCl_3$ were taken. Duration of experiment 10 hours. 195 ml dimethylaniline was recovered. Yield 25 g (42.9%) of (II).

(II) is a crystalline substance with b. p. 205-210° (5 mm), m. p. 67° [4, 7]. It crystallizes from alcohol as silvery white needles which turn pink in the air. It dissolves readily in organic solvents.

Found %: C 80.64; H 8.55; N 10.36. $C_{18}H_{24}N_2$. Calculated %: C 80.60; H 8.58; N 10.36.

Methoiodide m. p. 187-188°; picrate m. p. 146-147°; dihydrochloride m. p. 224-225° [8]; dinitro derivative m. p. 195° [4].

Deamination of (II). 120 g of 3% sodium amalgam was introduced in small portions with mechanical stirring in the course of 3 hours into an aqueous alcoholic solution of methoiodide [prepared from 4 g (II) and 3 ml methyl iodide] heated on a boiling water bath. After removal of the mercury and unreacted methoiodide (2.7 g), the reaction mixture was extracted with ether and the latter washed with dilute hydrochloric acid. From the ethereal solution was isolated 0.7 g (25.8%) 1,1-diphenylethane:

B. p. 268-270° (730 mm), d_{20}^{20} 1.0030, n_D^{20} 1.5760 [9], MR_D 60.07. $C_{14}H_{14}$. Calculated 59.65.

Oxidation of the 1,1-diphenylethane with chromic oxide in glacial acetic acid gave benzophenone with m. p. 47-48°; oxime m. p. 143° [10].

Condensation of paraldehyde with dimethylaniline in presence of $AlCl_3$. 1) 33 g $AlCl_3$ was introduced in small portions with mechanical stirring over a period of 1 hour into a mixture of 13 ml paraldehyde and 63 ml dimethylaniline heated on a boiling water bath; stirring was then continued for another 2 hours. After cooling, the reaction mass was a solid, resinous clot. Treatment with hot acidified water converted it into a slurry which was made alkaline and then distilled with steam. The distillate (10 ml) was unreacted dimethylaniline. The residue was extracted with ligroine to give 34.9 g of crude products from which 24.6 g (43.9%) of (II) was isolated by fractional distillation.

2) Into a mixture of 13 ml paraldehyde and 26 ml dimethylaniline was introduced dropwise, with mechanical stirring, 4 ml of chlorosulfonic acid. The mixture was heated 5 hours. After separation of the unreacted dimethylaniline (13 ml), a crystalline mass was obtained (12.5 g) from which by vacuum distillation was isolated 9.6 g of (II) (70% of the theoretical yield calculated on the reacted dimethylaniline).

Condensation of acetylene with dimethylaniline in presence of $AlCl_3$ in nitrobenzene. Acetylene was passed into a solution of 63 ml dimethylaniline in 100 ml nitrobenzene with mechanical stirring, and at the same time $AlCl_3$ (33 g) was introduced in small portions; the $AlCl_3$ dissolved in the mixture with considerable heat development and with change of color. After the $AlCl_3$ had been added, the reaction mixture was heated on a boiling water bath. The duration of the reaction was 7 hours. After removal of the nitrobenzene and unreacted dimethylaniline (15 ml) by steam distillation, first from the acid solution and then from the alkaline solution, 25 g of crude product was obtained from which by fractional distillation was isolated 15.5 g (32.1 %) of (V). B. p. 218-220° (6 mm); m. p. 89°.

Found %: C 79.95; H 8.66; N 11.91. $C_{13}H_{22}N_2$. Calculated %: C 80.31; H 8.66; N 11.02.

Picrate m. p. 177°; methoiodide m. p. 173-174° [11].

Deamination of (V) yielded diphenylmethane:

B. p. 256°, d_{20}^{20} 1.0055, n_D^{20} 1.5765 [12], MR_D 55.03; calc. 55.32; dinitrodiphenylmethane m. p. 181-182° [13].

Oxidation of diphenylmethane gave benzophenone, m. p. 48°, and its oxime, m. p. 143° [10].

The residue after separation of (V) was distilled to give a fraction with a very indefinite boiling point of about 280° (5 mm) [yield 3.8 g (8.07%)], in the form of a thick liquid which crystallized when stirred with alcohol; the compound was (VI); m. p. 173° [14]. Sometimes the residue was digested with chloroform, from which (VI) was brought down with methanol. Oxidation of (VI) with lead peroxide in acetic acid solution gave crystal violet.

Condensation of acetylene with dimethylaniline in presence of $SnCl_4$. Dropwise addition was made in 5 hours of 22.8 g $SnCl_4$ to 63 ml dimethylaniline heated on a boiling water bath; at the same time acetylene was passed in at a speed of 10 liters per hour; the mixture was mechanically stirred. The products comprised 42 ml unchanged dimethylaniline, 9.2 g (43.6%) (V) and 3.3 g (16%)(VI).

SUMMARY

1. Condensations of dimethylaniline with acetylene in presence of $AlCl_3$ go in the same manner as with other aromatic compounds. 1,1-Di-(4-dimethylaminophenyl)-ethane is obtained in a yield of 43% of the theoretical.

2. Condensations of acetaldehyde with dimethylaniline in presence of acid catalysts go as dehydration reactions and lead to substance (II). By using chlorosulfonic acid as catalyst, a yield of 70% (on the reacted dimethylaniline) of (II) is obtained.

LITERATURE CITED

[1] I. P. Tsukervanik, Proc. Acad. Sci. USSR 74, 959 (1950); I. P. Tsukervanik and T. G. Garkovets, J. Gen. Chem. 25, 919 (1955) (T.p. 883).*

[2] O. W. Cook and V. J. Chambers, J. Am. Chem. Soc. 43, 334 (1921).

[3] A. E. Chichibabin, J. Russ. Chem. Soc. 47, 713 (1915); N. S. Kozlov et al., J. Gen. Chem. 6, 250, 1341, 1349, 1352, 1897, 1936 (1936); 7, 51, 54, (1937); L. E. Olifson, Bull. Chkalov Div. All-Union Chem. Soc. 3, 39 (1949); Comm. Sci. Work Members of the Mendeleev Chem. Soc. 1949, No. 3, 40; I. F. Kryuk, J. Gen. Chem. 10, 1507 (1940).

[4] A. Trillat, Bull. soc. chim. (3), 23, 18 (1900).

[5] I. P. Tsukervanik and T. G. Garkovets, Author's Certificate No. 75717 (1949).

[6] H. Meyer, Detection and Determination of Organic Compounds (United Sci. Tech. Press, 1937), 528; Houben, Methods of Organic Chemistry (State Chem. Press, 1949), 4, 785.

[7] M. Freund and F. Mayer, Ber. 39, 1117 (1906).

[8] A. Trillat, Chem. Zentr. 1899, II, 203.

[9] Dict. Org. Compounds I, 1027.

[10] Ibid. I, 225, 226.

[11] Ibid. III, 726.

[12] Ibid. I, 1034.

[13] W. H. Doer, Ber. 5, 795 (1872).

[14] Beilst. 13, 315.

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* T.p. = C. B. Translation pagination.

SYNTHESIS OF 1,4-DIAMINOBUTANONE-2

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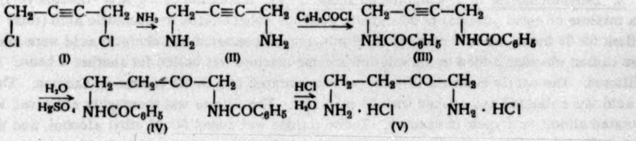
1,4-Diaminobutanone-2 is an important intermediate in the synthesis of histamine, but a really convenient method of synthesis had not been developed until recently. 1,4-Diaminobutanone-2 was first prepared by Pyman in 1929 by hydrolysis of N,N'-dibenzoyl-1,4-diaminobutanone-2 with hydrochloric acid under pressure [1]; this method, however, is only of theoretical value since the N,N'-dibenzoyl-1,4-diaminobutanone-2 itself was obtained from natural histamine.

In 1952 Fraser and Raphael [2] obtained the dihydrochloride of 1,4-diaminobutanone-2 by the following series of reactions: 1,4-diphthalimidobutine-2, prepared from potassium phthalimide and 1,4-dichlorobutine-2, was hydrated under the conditions of the Kucherov reaction, and hydrolysis of the resultant 1,4-diphthalimidibutanone-2 with hydrochloric acid gave the dihyrochloride of 1,4-diaminobutanone-2.•

Another (not sufficiently practical) synthesis of 1,4-diaminobutanone-2 was described in 1953. This started from phthalimidoacetyl chloride and involved subsequent enlargement of the carbon chain with the help of diazomethane [3].

In the present work, 1,4-diaminobutanone-2 was obtained by the following route: reaction of 1,4-dichlorobutine-2 (I) with ammonia gave 1,4-diaminobutine-2 (II) (yield 37%); action of benzoyl chloride on (II) gave N,N'-dibenzoyl-1,4-diaminobutine-2 (III) (yield 90%); hydration of the latter in presence of mercuric sulfate led to N,N'-dibenzoyl-1,4-diaminobutanone-2 (IV) (yield 72%), hydrolysis of which by prolonged boiling with a mixture of acetic and hydrochloric acids gave the dihydrochloride of 1,4-diaminobutanone-2 (V) (yield 65%).


$CH_2-C\equiv C-CH_2$ (Cl, Cl) (I)
NH_3
$CH_2-C\equiv C-CH_2$ (NH_2, NH_2) (II)
C_6H_5COCl
$CH_2-C\equiv C-CH_2$ ($NHCOC_6H_5$, $NHCOC_6H_5$) (III)
H_2O, H_2SO_4
$CH_2-CH_2-CO-CH_2$ ($NHCOC_6H_5$, $NHCOC_6H_5$) (IV)
HCl, H_2O
$CH_2-CH_2-CO-CH_2$ ($NH_2 \cdot HCl$, $NH_2 \cdot HCl$) (V)

Hydration of (III) with formation of (IV) is of special interest in itself because, apart from the work of Fraser and Raphael [2], the literature only describes unsuccessful attempts to hydrate acetylenic compounds containing an amino group adjacent to a triple bond [4].

Our proposed method of synthesis of 1,4-diaminobutanone-2 only comprises four steps, three of which (apart from the first) go with perfectly satisfactory yields of reaction products and with good reproducibility of results; we therefore recommend this method for the synthesis of 1,4-diaminobutanone-2.

EXPERIMENTAL

1. 1,4-Diaminobutine-2 (II) [4]. A mixture of 51 g freshly distilled 1,4-dichlorobutine-2 and 2 liters

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• The paper of Fraser and Raphael evidently omitted full details of the preparation; our numerous attempts to repeat the preparation gave negative results (potassium phthalimide did not enter into reaction with 1,4-dichlorobutine-2).

concentrated aqueous ammonia was stirred for 8 hours in a round-bottomed flask (3 liters capacity). The next day the solution was evaporated on a water bath until the ammonia odor had disappeared; the residue was acidified with concentrated hydrochloric acid (congo test) and again evaporated nearly to dryness. To the residue was added 200 ml 10 N sodium hydroxide solution until strongly alkaline, and the resultant 1,4-diaminobutine-2 was extracted for 70 hours with ether in an extractor. After driving off the ether, the residue was distilled in vacuum to give 13 g (37%) 1,4-diaminobutine-2; b. p. 82-84° (6 mm); m. p. 41-43°.

Literature data: b. p. 60-80° (11 mm), m. p. 42-46° [4].

2. N, N'-Dibenzoyl-1,4-diaminobutine-2 (III). To a solution of 5.4 g 1,4-diaminobutine-2 in 360 ml 10% potassium hydroxide was gradually added 18.4 g benzoyl chloride. The mixture was shaken 3 hours on a rocker, after which the precipitate was collected, heated 10 minutes with 10% potassium hydroxide solution, again separated, washed on the filter with hot water, and dried at 80°. Yield 16.9 g N,N'-dibenzoyl-1,4-diaminobutine-2 (90.3%); m. p. (from alcohol) 210°.

Found %: C73.61, 73.83; H 5.74, 5.76; N 9.84, 9.84. $C_{18}H_{16}O_2N_2$. Calculated %: C 73.95; H 5.52; N 9.58.

N,N'-Dibenzoyl-1,4-diaminobutine-2 has not been described in the literature.

3. N,N'-Dibenzoyl-1,4-diaminobutanone-2 (IV). 6 g mercuric sulfate was added to a solution of 15 g N,N'-dibenzoyl-1,4-diaminobutine-2 in 900 ml 90% acetic acid; the mixture was left overnight and then heated for 20 hours on a water bath in a flask with a reflux condenser at a bath temperature of 70-80°. After filtration, the solvent was distilled off until the residue was nearly dry; 300 ml water was added, and after 30 minutes the crystals were separated. Yield 11.5 g (72%) N,N'-dibenzoyl-1,4-diaminobutanone-2; m. p. 157-158° (from 75% alcohol).

Found %: C 69.78, 69.96; H 6.03, 6.16; N 9.37, 9.38. $C_{18}H_{18}O_3N_2$. Calculated %: C 69.66; H 5.84; N 9.02.
Semicarbazone m. p. 171-172°.
Literature data for (IV): m. p. 157-158° [1], 151° [5]; semicarbazone m. p. 172-173° [5].

4. Dihydrochloride of 1,4-diaminobutanone-2 (V). A solution of 3 g N,N'-dibenzoyl-1,4-diaminobutanone-2 in a mixture of equal volumes of 98% acetic acid and concentrated hydrochloric acid (total 150 ml) was refluxed in a flask for 30 hours, while 4 portions of 10 ml each concentrated hydrochloric acid were added at intervals. Active carbon was then added to the solution and the mixture was boiled for another 4 hours; it was then cooled and filtered. The nearly colorless filtrate was concentrated to a small volume in vacuum. The separated benzoic acid was collected and washed with 10 ml water. The filtrate was thoroughly extracted with ether and again evaporated almost to dryness in vacuum. To the residue was added 35 ml ethyl alcohol, and the mixture was cooled to 0°. The white, crystalline precipitate was collected, washed with a little alcohol and ether and dried in a vacuum desiccator. Yield 1.1 g dihydrochloride of 1,4-diaminobutanone-2 (65%); m. p. 215-216° (decomp.).

Found %: N 16.11, 16.30. $C_4H_{12}ON_2Cl_2$. Calculated %: N 16.00.
Literature data: m. p. 221° (decomp.) [1]; 217° (decomp.) [2]; 220-221° (decomp) [3].

SUMMARY

1,4-Diaminobutanone-2 can be prepared from 1,4-diaminobutine-2 by benzoylation, hydration and subsequent hydrolysis of N,N'-dibenzoyl-1,4-diaminobutanone-2. The method can therefore be used for the synthesis of 1,4-diaminobutanone-2.

LITERATURE CITED

[1] F. Pyman, J. Chem. Soc. (1930), 98; British Patent No. 325151 (1929); C. A. 24, 3861 (1930).

[2] M. Fraser and R. Raphael, J. Chem. Soc. 1952, 226.

[3] J. Michalsky, J. Borkovec and H. Hadacek, Chem. Listy 47, 1239 (1953).

[4] A. Johnson, J. Chem. Soc. 1946, 1009.

[5] A. Windaus, W. Dorries and H. Jensen, Ber. 54B, 2745 (1921).

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II. THE CATALYTIC TRANSFORMATION OF n-BUTYL ALCOHOL UNDER PRESSURE

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Investigation of the transformation of ethyl alcohol over copper activated catalyst showed that the direction of the reactions taking place at the catalyst is governed not only by the temperature but also by the pressure [1]. At 300-340° and pressures up to 10 atm., the main products are ketones, while at 350-400° and pressures of 20-150 atm. they are saturated hydrocarbons corresponding in number of carbon atoms to the ketones obtained at atmospheric pressure. Higher hydrocarbons (n-heptane, octane, etc.) are obtained at 10-20 atm., and lower hydrocarbons (propane and n-pentane) at pressures above 20 atm.

An earlier study of the catalytic transformation of n-butyl and other primary alcohols at normal pressure over the same copper catalyst [2, 3] showed that symmetrical ketones are formed in 50% yield (on the original alcohol) at temperatures of 325-350° and a space velocity of 150. The very much higher content of carbon monoxide in the gas (compared with the CO_2 content) indicated that ketones are formed from alcohols through intermediate formation of aldehyde and aldol.

The present work concerns the conditions of transformation of n-butyl alcohol over copper activated catalyst [4, 5] under pressure. The investigations established that the direction of reaction in this case, as in that of ethyl alcohol, depends upon the temperature and pressure. At the ordinary pressure and at temperatures of 325-350°, butyl alcohol is quantitatively transformed into dipropyl ketone, while at higher pressures up to 15 atm. the product is n-heptane. Increase of pressure from 15 to 80 atm. markedly reduces the yield of n-heptane.

EXPERIMENTAL

Experiments were carried out in the high-pressure apparatus described in the preceding communication [1]. Alcohol and hydrogen were continuously fed into the reactor in 1 : 1 molar ratio. The catalyst was No. 1 copper catalyst activated with thorium oxide and reduced with hydrogen at 285-300° and atmospheric pressure.

the condensates obtained were subjected to fractional distillation and analyzed for their content of aldehyde, ester, acid, ketones, and saturated and unsaturated hydrocarbons.

The composition of the gas and its yield, allowing for the gases condensed in the traps (temperature −70°), was calculated after deducting the hydrogen fed into the reactor during the experiment.

With the objective of establishing the effect of temperature on the direction of the reactions taking place at the catalyst, a series of experiments was run at a pressure of 15 atm. Results are presented in Table 1 and Fig. 1. At temperatures of 300-360° the amounts of butyl butyrate and dipropyl ketone in the condensate fell sharply and the yields of saturated hydrocarbons and water increased. The maximum yield of saturated hydrocarbons is obtained at 340-360°. Under these conditions the main product from n-butyl alcohol is n-heptane (70-75% in the condensate). A considerable proportion of 3-methylheptane was found among the higher hydrocarbons.

Rise of temperature to 410° is accompanied by fall in the hydrogenating properties of the catalyst, and the yield of saturated hydrocarbons falls sharply. The condensate contains more ketones, and part of the alcohol does not enter into reaction.

A very small amount of water is detected (50% of theory in relation to the hydrocarbons obtained) when there is a relatively high content of n-heptane and other hydrocarbons in the condensate. This may be accounted for by the data of Tables 1 and 2, which characterize the composition and yield of the gaseous products; the latter contain much propane, evidently due to decomposition of butyraldehyde: $C_3H_7CHO \rightarrow C_3H_8 + CO$. The high CO_2 content (30%) of the gas and the low carbon monoxide content (3-5%) and the presence of an insignificant amount of water in the reaction products may be due to the water gas reaction taking place at the catalyst:

$$CO + H_2O \rightleftharpoons CO_2 + H_2.$$

TABLE 1

Catalytic Transformation of n-Butyl Alcohol at 15 atm. Pressure

Temperature	Yield (in weight %)		Yield (in weight %) related to the original alcohol												
	of condensate	of gas	of butyraldehyde	of heptane	of dipropyl ketone	of butyl butyrate	of water	of higher ketones	of higher hydrocarbons	C_3H_8	C_4H_8	C_4H_{10}	CO_2	CO	H_2
305°	81.0	16.0	1.1	15.6	18.8	6.7	0.0	1.0	3.0	0.2	0.0	1.0	10.0	3.0	2.0
340	60.0	40.0	0.0	43.3	1.6	1.3	5.1	0.2	3.9	3.0	1.0	16.0	20.0	6.0	1.0
360	65.2	33.7	0.0	43.8	1.6	0.0	5.7	0.0	4.9	5.8	0.0	4.5	17.4	5.0	1.0
385	68.5	23.0	0.0	34.0	3.6	0.0	7.6	0.5	11.4	1.0	0.0	2.0	13.0	5.0	2.0
410	66.7	20.0	1.0	3.1	10.0	0.5	5.3	16.3	7.0	2.0	2.0	1.0	7.0	5.0	2.2

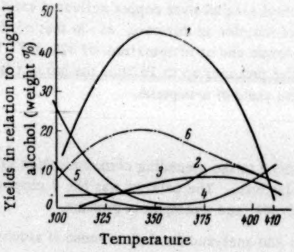


Figure 1. Effect of temperature on yields of reaction products at a pressure of 15 atm.
1) n-Heptane, 2) higher hydrocarbons, 3) water, 4) dipropyl ketone, 5) butyl butyrate, 6) CO_2.

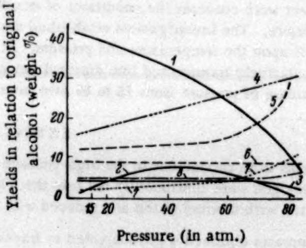


Figure 2. Influence of pressure on yields of products of reaction at 350°.
1) n-Heptane, 2) dipropyl ketone, 3) water, 4) CO_2, 5) propane, 6) butylene, 7) butane, 8) carbon monoxide.

Butylene and butane were also detected in the gas; their formation is evidently associated with reactions of dehydration and hydrogenation of the alcohol.

Another series of experiments was performed at 350° and pressures of 15 to 80 atm. These experiments particularly clearly demonstrated the development of the above mentioned secondary reactions, leading to suppression, at 340-360° and 15 atm., of the formation of n-heptane.

With rise of pressure the yield of n-heptane from butyl alcohol fell by a factor of 4, and the yields of CO_2, propane and butane increased considerably. Results at 350° and various pressures are presented in Table 2 and Fig. 2.

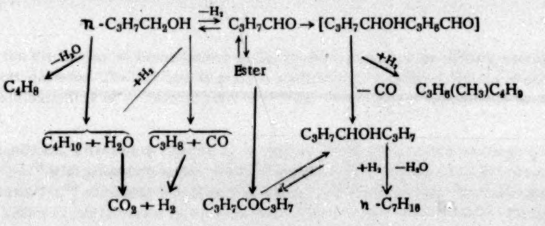
TABLE 2

Influence of Pressure on the Catalytic Transformation of n-Butyl Alcohol at 350°

Pressure (in atm.)	Yield (in weight %)		Yields (in weight %) reckoned on original alcohol											
	of condensate	of gas	of butyraldehyde	of heptane	of dipropyl ketone	of butyl butyrate	of higher hydrocarbons	of water	C_3H_8	C_4H_8	C_4H_{10}	CO_2	CO	H_2
15	56.8	40.0	0.1	40.0	2.4	2.0	9.0	3.1	12.0	3.0	2.0	17.0	4.0	2.0
40	65.4	35.0	0.1	33.0	7.7	5.0	8.9	3.7	5.0	1.0	3.0	22.0	8.0	1.0
60	50.0	40.0	0.0	24.0	4.5	1.4	8.0	3.6	15.0	1.0	3.0	14.0	4.0	3.0
80	27.0	77.0	0.0	10.2	1.4	1.5	9.0	2.7	27	3.0	10.0	30.0	6.0	1.0

At a pressure above 40 atm. there is a marked retardation of condensation of the aldehyde (originally formed from butyl alcohol) which leads to aldol, as well as of its transformation into n-heptane; at the same time the catalytic cracking of the butyraldehyde and the carbon monoxide conversion are accelerated. This leads to increased yields of propane and CO_2. The presence in the reaction products of a considerable amount of water in association with a low yield of liquid hydrocarbons indicates hydrogenation of the butyraldehyde at high pressures (40-80 atm.) and leads to formation of butane, which was detected in adequate amount in the condensate trapped at low temperature (−70°).

The catalytic reactions of transformation of n-butyl alcohol, taking place at the catalyst when the process is conducted under pressure, may be represented by the following scheme:



Constants of the identified saturated hydrocarbons are set forth in Table 3.

TABLE 3

Hydrocarbon	Determined			Literature data [6]	
	Molecular weight	Boiling point	n_D^{20}	Boiling point	n_D^{20}
n-Heptane	101	98°	1.3880	98.4°	1.3877
3-Methylheptane	113.0	116-117	1.3980	118.9	1.3985

SUMMARY

1. n-Butyl alcohol is transformed into n-heptane in 40-45% yield at 340-360° and a pressure of not more than 15 atm. over copper activated catalyst.

2. At pressure higher than 15 atm. the formation of n-heptane from butyl alcohol is markedly reduced due to intensification of secondary reactions (cracking of butyraldehyde and hydrogenation of the latter to butane).

3. The presence of much water in the reaction products leads to catalytic conversion of carbon monoxide to CO_2.

LITERATURE CITED

[1] B. A. Bolotov and L. K. Smirnova, J. Gen. Chem. 25, 1987 (1955) (T.p. 1933).*

[2] B. A. Bolotov et al., J. Appl. Chem. 28, 516 (1955) (T.p. 489).*

[3] Ibid., p. 414 (T.p. 391).*

[4] Ibid., p. 71 (T.p. 61).*

[5] B. A. Bolotov and B. N. Dolgov, Author's Declaration No. 92622 (1950).

[6] S. Milliken, Identification of Pure Organic Compounds (1946).

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* T.p. = C. B. Translation pagination.

THE ISOMERIZATION OF MONODEUTERONAPHTHALENES

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and P. Alikhanov

A characteristic feature of the α-derivatives of naphthalene is their susceptibility under certain conditions to isomerization into β-derivatives. This phenomen was first observed in the case of naphthalene-α-sulfonic acid [1]. Later investigators reported the isomerization of α-alklyl-, α-aryl-, and α-halo- derivatives of naphthalene [2].

Isomerization of naphthalene-α-sulfonic acid is observed on heating the α-isomer with sulfuric acid. α-Alkyl-, α-aryl-and α-halo- derivatives of naphthalene, with the exception of α-fluoronaphthalene [3], isomerize when their vapor is passed over silica gel and other catalysts in a gas stream at high temperature.

A nucleophilic substitution reaction in the naphthalene series leads in isolated cases to formation of isomeric compounds. Thus, for example, with potassium amide in liquid ammonia, α-chloro-, bromo- and iodonaphthalenes form β-naphthylamine (fluoronaphthalene is an exception [4]; under the same conditions it forms α-naphthylamine); α-bromo-, chloro- and fluoronaphthalenes with lithium diethylamide in an ether medium form β-diethylnaphthylamine [5]; heating of α-chloronaphthalene with 4-toluidine in presence of soda lime leads to N-tolyl-β-naphthylamine; under the same conditions, α-bromonaphthalene with aniline forms N-phenyl-β-naphthylamine.*

From this standpoint, attention is merited by an observation of the isomeric rearrangement during reaction of chlorobenzene-1-C^{14} with potassium amide in liquid ammonia [8]. The author of the paper showed that about 50% of aminobenzene-1-C^{14} and about 50% of aminobenzene-1-C^{12} are formed. The formation of the two anilines enabled the author to put forward a new mechanism of the reaction of nucleophilic kinesubstitution. He suggests that the formation of aniline is preceded by loss by chlorobenzene of the elements of hydrogen chloride. This leads to a labile compound, C_6H_4, and then to addition of the elements of ammonia with formation of aniline. On this basis we can explain the many nucleophilic kinesubstitution reactions in the series of naphthalene, benzene, dibenzofuran and dibenzothiophene. (For a list of examples of nucleophilic kinesubstitution see [9]. In the present paper we put forward other theories of the mechanism of nucleophilic kinesubstitution.)

The formation of cyclohexadienine, C_6H_4, by reaction of o-fluorobenzene with lithium amalgam in a furan medium has recently been demonstrated. This labile dienophile then reacts with furan to form the adduct 1,4-dihydronaphthalene-1,4-endoxide in a yield of up to 76%. The adduct isomerizes to α-naphthol under the action of hydrochloric acid [10].

With the objective of studying cases of isomerism in the naphthalene series from the standpoint of formation of the labile C_6H_4, we decided it would be of interest to investigate the isomerism of monodeuteronaphthalenes. We considered that the formation of $C_{10}H_6$ and subsequent addition of the elements protium and deuterium ought to lead to an equimolecular mixture of α- and β-deuteroanilines. (A. Korolev and E. Yurygina.)

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* Elucidation of the mechanism of isomerization in the naphthalene series necessitates consideration of at least all the examples cited above. The attempts of many investigators to consider individual mechansims, for example of the isomeric transformations of α-sulfonic acids or β-halo- derivatives of naphthalene do not appear to us to be convincing [7].

In the present work we studied the possibility of migration of hydrogen in the naphthalene molecule. We made use of deuterium. Little is known about the migration of hydrogen in aromatic hydrocarbons. A study of toluene in this connection showed that prolonged heating of its ortho-deutero- derivative did not lead to translocation of the hydrogen atoms [11].

For the evaluation of migration of hydrogen in the naphthalene molecule, we made use of the fact that the rates of isotopic exchange of the α- and β-atoms of hydrogen in naphthalene with deuterium bromide are different. This conclusion was previously reached [12] on the basis of analysis of the kinetic curve, and it was confirmed in the present work by measurements of the rate of reciprocal exchange with liquid hydrogen bromide of the deuterium of α- and β-monodeuteronaphthalenes. It was found that at 25° the velocity constant of exchange of deuterium with hydrogen is: for the α-isomer $k = 2\text{-}3 \cdot 10^{-3}\,\text{sec}^{-1}$; for the β-isomer $k = 5 \cdot 10^{-5}\,\text{sec}^{-1}$.

We compared the rate of hydrogen exchange in preparations of monodeuteronaphthalenes heated to 400 ± 10° for 52 hours and in control preparations which were not subjected to heat treatment. In these experiments we established the absence of hydrogen migration in the naphthalene molecule.

Migration of hydrogen both from the α- to the β-position and from the β- to the α-position was established on passing the vapors of α- and β-monodeuteronaphthalenes in a stream of nitrogen over silica gel at 420°. Under the test conditions we obtained a mixture of approximately equal parts of α- and β-isomers. Incidentally, we showed that also in the case of methyl derivatives of naphthalene there is migration of the methyl group, not only from the α- to the β-position, as was established previously [2], but also from the β- to the α-position. Consequently, the migration of hydrogen and of the methyl group also proceeds reversibly under similar conditions, the only difference being that hydrogen migrates with great facility than the methyl group.

EXPERIMENTAL

α- and β-monodeuteronaphthalenes were prepared as described earlier [13]. The purity of the substances used in the syntheses was checked by analyses and by measurements of constants (see Table 5). The preparations were recrystallized from a gasoline fraction and twice sublimed in vacuum. *

Heating of the preparations of monodeuteronaphthalenes. Weighed samples of about 1 g of α- and β-monodeuteronaphthalenes were sealed into evacuated ampoules and heated for 52 hours at 400 ± 10°. The melting point had not changed after the heating. The compounds were sublimed prior to the hydrogen exchange reaction.

Passage of vapor of monodeuteronaphthalene over silica gel. The isomerization reaction was performed in a glass tube, length 100 cm and inside diameter 16 mm, placed in a vertical electric furnace. The catalyst was a large-pore silica gel (KSK grade of the Voskresensky works). The height of the catalyst bed was 65 cm. The volume was about 100 ml. A 10 cm bed of glass rings, serving as vaporizer, was placed above the catalyst bed in the upper part of the tube. The compound was fed into the tube at a rate of 1 g per 10-20 minutes in a nitrogen stream which was introduced at a speed of 8-10 ml/min. During the experiment the temperature was held at 420 ± 5°. The catalyzate was purified by 4-5 distillations in vacuum.

Hydrogen exchange experiments. Weighed amounts (about 0.2 g) of monodeuteronaphthalene were sealed into thin-walled ampoules and placed in test tubes connected by ground-glass joints to an apparatus for the preparation of hydrogen bromide from carefully purified hydrogen and chemically pure bromine. The HBr was thoroughly purified from excess of Br_2. About 20 g liquid HBr was condensed into each of the test tubes. The tubes were then sealed and placed in a thermostat (25 ± 0.1°). The ampoules were crushed by the vapor pressure of the liquid HBr and the monodeuteronaphthalene rapidly dissolved in the HBr. Colorless solutions were obtained. After a definite period of time, the test tubes were taken out of the thermostat and immersed in liquid air. Afterwards, the test tubes were opened and the HBr evaporated. The residual naphthalene was purified by sublimation. The melting point had not altered. The naphthalene was burnt in a special furnace for rapid combustion; the water formed was purified by addition of BaO and distillation in vacuum; its density was measured by the drop method and the isotopic composition of the naphthalene was thereby determined.

Comparison of the rate of hydrogen exchange in isomers of monodeuteronaphthalene. ** Results of experiments on hydrogen exchange between α- and β-monodeuteronaphthalene and liquid hydrogen bromide are presented in Tables 1 and 2. The following symbols are employed: t_1 – duration of heating at 400° (in hours); t_2 – duration of exchange experiment (hours); P_B – weight of monodeuteronaphthalene (in g); P_P – weight of hydrogen bromide; M – number of moles of hydrogen bromide per mole monodeuteronaphthalene; C_B^0 – concentration of deuterium in the water from combustion of the naphthalene before the experiment (at. %); C_B – concentration of deuterium in the water from combustion of naphthalene after experiment (at. %).

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* In preliminary experiments the recrystallization and sublimation were carried out at room temperature.

** We express our thanks to M. B. Neiman for advice on carrying out the experiments on reciprocal exchange with isomers of monodeuteronaphthalene.

A comparison of the results in Tables 1 and 2 shows that in the α-isomer the exchange of deuterium with hydrogen is considerably faster than in the β-isomer.

TABLE 1

Experiments With α-Monodeuteronaphthalene
($t_1 = 0$)

t_2	P_B	P_p	M	C_B^0	C_B
0.25	0.199	16.6	130	10.1	1.73
0.25	0.180	16.0	140	10.8	2.12
0.25	0.180	16.4	145	10.8	2.33
0.25	0.179	13.3	120	10.8	2.09
0.5	0.200	20.5	160	10.1	1.05
0.5	0.200	19.9	160	10.1	1.05
0.5	0.200	21.5	170	10.1	1.03
0.5	0.201	23.5	190	10.1	0.92
1	0.181	18.6	160	10.8	1.64
1	0.180	17.2	150	10.8	1.68
1	0.181	18.9	170	10.8	1.68
25	0.201	16.6	130	10.1	1.51
25	0.202	21.1	165	10.1	1.22

TABLE 2

Experiments with β-monodetueronaphthalene
($t_1 = 0$)

t	P_B	P_p	M	C_B^0	C_B
0.5	0.214	19.9	150	10.3	9.3
0.5	0.258	15.8	100	10.3	9.3
0.5	0.275	15.8	90	10.3	9.5
0.5	0.203	12.4	200	10.3	9.3
0.5	0.212	17.3	130	10.3	9.2
0.5	0.238	17.7	120	10.3	9.2
0.5	0.200	17.3	140	10.4	9.65
0.5	0.201	17.7	140	10.4	9.56
0.5	0.203	17.8	140	10.4	9.58
0.5	0.201	18.1	140	10.4	9.58
25	0.202	16.3	130	10.4	1.59
25	0.206	18.5	140	10.4	1.53

The following first-order equation may be used for calculation of the velocity constant of exchange of deuterium in the substance with the hydrogen of the solvent:

$$k = \frac{2.3}{t}\log\frac{C_B^0 - C'_{B(act.)}}{C_{B(act.)} - C'_{B(act.)}},$$

in which t is the duration of the kinetic experiment in seconds; C_B^0, C_B and C'_B are respectively, the concentrations of deuterium in the water of combustion of the naphthalene preparation before the start of the experiment, the concentration in the water of combustion of the naphthalene isolated after time t, and the concentration after attainment of equilibrium of the exchange reaction. The concentrations with the subscript (act.) differ from those observed because part of the deuterium passing from the substance into solution again enters the substance due to the fact that hydrogen atoms of naphthalene in the α-position easily exchange with deuterium, which gradually accumulates in the solvent.

In the calculation of k it must be remembered that equilibrium is established after only an hour and that $C_{B(act.)} = C'_B/4$. The correction is $\Delta C_B = C_B - C_{B(act.)} = f(t_1, v_1, v_2, \alpha)$, where v_1 and v_2 are the velocity of passage of deuterium from the substance into the solvent and, conversely, α is the coefficient of distribution of deuterium between substance and solvent. C_B can vary between 0 and $\frac{3}{4}C'_B$. Correspondingly the velocity constant $k\alpha$ will vary in the range of $2\text{-}3^{-3} \cdot \text{sec}^{-1}$. This correction may be avoided by carrying out the reciprocal exchange experiments with α-tetradeuteronaphthalene.

When calculating the velocity constant of isotopic exchange of the β atom, we assume that when equilibrium is established (after 25 hours), $C'_{B(act.)} = C'_B/8$. With a short-period experiment (30 minutes), the exchange of deuterium between solvent and β-C—H bonds may be neglected.

As was shown by a trial calculation, the correction due to partial passage of deuterium from solution into the α-C—H bonds of naphthalene ΔC_B is less than 0.06 atom.% D and it can be neglected.

$k_\beta = 5 \cdot 10^{-5}$ sec^{-1}, i. e., 40 to 60 times smaller than k_α, in agreement with the ratio of these constants that was previously found on the basis of analysis of the kinetic curve of direct exchange [8].

Absence of isomerization on heating. Table 3 gives the results of experiments on isotopic exchange carried out with naphthalene preparations at 400 ± 10° for 52 hours.

TABLE 3

Experiments on Hydrogen Exchange with Preparations of Monodeuteronaphthalene Subjected to Heating ($t_1 = 52$; $t_2 = 0.5$)

p_B	p_p	M	c_B^0	c_B
		α-Monodeuteronaphthalene		
0.199	20.1	160	10.1	0.95
0.198	21.2	170	10.1	1.00
0.200	21.1	170	10.1	1.03
0.212	21.4	160	10.1	0.95
		β-Monodeuteronaphthalene		
0.198	15.6	125	10.4	9.58
0.198	21.1	170	10.4	9.58
0.192	14.6	120	10.4	9.32
0.200	16.5	130	10.4	9.43

In Table 4 the values of C_B from experiments carried out with both isomers of monodeuteronaphthalene under identical conditions (duration of exchange 0.5 hour at 25°) are compared.

TABLE 4

Comparison of Results Obtained with the Heated and the Control Preparations

	M	c_B^0	c_B	c_B^0/c_B
		α-Monodeuteronaphthalene		
Without heating . . .	160–190	10.1	1.01 ± 0.05	10.0
With heating . . .	160–170	10.1	0.98 ± 0.04	10.1
		β-Monodeuteronaphthalene		
Without heating	140	10.4	9.59 ± 0.04	1.1
With heating . . .	120–170	10.4	9.48 ± 0.10	1.1

Consequently, the rate of hydrogen exchange within the limits of experimental error is the same, i. e., the heating of naphthalene is not accompanied by migration of deuterium atoms from the α-position into the β-position or conversely.

Isomerization of monodeuteronaphthalene over silica gel. In view of the circumstance that in experiments with methylnaphthalenes (see below) the equilibrium of the isomerization reaction was only attained after numerous passages over the catalyst, α-monodeuteronaphthalene in a first series of experiments was subjected to 11 passes over the catalyst (preparation no. 1), and part of the substance was exposed another 4 times to the catalyst (preparation no. 2).

In the second (principal) series of experiments the vapor of α-monodeuteronaphthalene was passed over silica gel 3, 6 and 12 times (preparations no. 3 to 5), and the vapor of β-monodeuteronaphthalene was passed over the catalyst 6 times (preparation no.8). In a third series of experiments, both isomers were passed over the catalyst once and twice (preparations 6 and 7). Results of the isomerization experiments are presented in Table 5.

TABLE 5

Experiments on Isomerization of Monodeuteronaphthalene

Preparation No.	Isomer	Number of passes over catalyst	Weight of substance		Melting point		Conc. of D (at. %)	
			initial	final	initial	final*	initial	final
1	α	11	8.0	4.3	80.7—81.0	80.7—81.1	11.4	4.9
2	α	(11) + 5	1.6	0.9	80.7—81.0	80.5—80.9	4.9	1.65
3	α	3	21	15.6	80.8—81.5	79.8—80.2	10.06	9.80
4	α	(3) + 3	13	9.0	79.8—80.2	80.1—80.5	9.80	5.51
5	α	(3 + 3) + 6	6.5	3.9	80.1—80.5	80.0—80.3	5.51	3.98
6	α	1	8.0	7.7	80.4—81.1	80.0—80.7	10.5	9.1
7	α	2	4.4	4.1	80.0—80.7	79.8—80.2	—	9.4
8	β	6	6.0	4.4	80.0—80.3	80.0—80.4	10.44	7.28
9	β	1	7.0	6.6	80.0—80.6	80.0—80.5	9.9	8.6
10	β	2	3.6	3.2	80.0—80.5	80.1—80.4	—	8.7

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* After purification.

We observed a gradual fall in the deuterium content when monodeuteronaphthalene vapor was passed over heated silica gel (for example, after 12 passes the concentration of deuterium fell from 11.4 to 1.65 at. %). It may be thought that this is associated with silica gel-catalyzed exchange between deuteronaphthalene and the products of its cracking formed during the experiment. We did not study this process more closely.

The catalyzate is a mixture of a crystalline and an amorphous product with a yellow color. After purification by 3-5 distillations in vacuum, the substance has the same constants as the original substance. Hydrogen exchange experiments were run with the purified substances in order to establish the isometic composition of the products of the catalytic reaction. Results obtained with both isomers are given in Tables 6 and 7.

The results are seen to be the same, irrespective of the number of passes or of which of the isomer vapors was passed over the heated silica gel; no difference in exchange was observed after 30 minutes at 25°. The ratio $C_B^0/C_B = 1.9 \pm 0.1$.

Comparison with the data presented in Table 4 shows that passage of monodeuteronaphthalene vapors over heated silica gel results in the deuterium migrating both from the α - into the β -position and from the β - into the α -position. Equilibrium is established after only one pass.

In order to evaluate the concentration of each of the isomers in the equilibrium mixture, we assume that with a duration of the exchange reaction of 30 minutes, substantially only the deuterium in the α -position exchanges ($C_B^0 - C_B = C_B$). The percentage of α -isomer in the equilibrium mixture will then be given by the formula

$$\%\,\alpha = \frac{C_B \cdot 100}{C_B^0} = \frac{(C_B^0 - C_B) \cdot 100}{C_B^0},$$

according to our experiments $C_B^0 = 1.9\ C_B$; consequently,

$$\%\,\alpha = \frac{(1.9\ C_B - C_B) \cdot 100}{1.9\ C_B} = 47\%.$$

The concentration of α -isomer in the equilibrium mixture calculated in this way is slightly high.

Isomerization of methylnaphthalene over silica gel. Unlike Mayer [2], we carried out experiments with both isomers of methylnaphthalene and attempted to establish whether passage over the catalyst leads to equilibrium from both sides. The same procedure was used as with monodeuteronaphthalene. We used in an experiment

5 g α-methylnaphthalene (b. p. 105° at 8-9 mm) and 7 g β-methylnaphthalene (m. p. 33.9-34.0°). Results are given in Table 8.

TABLE 6

Hydrogen-Exchange Experiments with α-Deuteronaphthalene After Heating Over SiO_2

Preparation No.	t_1	P_B	P_p	M	C_B^0	C_B
1	0.5	0.200	17.6	140	4.9	2.6
1	0.5	0.215	16.4	120	4.9	2.6
1	0.5	0.212	9.2	70	4.9	2.7
1	0.5	0.179	10.6	90	4.9	2.7
2	0.5	0.174	13.9	130	1.65	0.88
2	0.5	0.196	16.1	130	1.65	0.86
2	0.5	0.166	12.3	120	1.65	0.82
3	0.5	0.200	17.2	140	9.80	4.10
3	0.5	0.200	14.8	160	9.80	4.10
3	22	0.200	18.2	145	9.80	1.15
3	22	0.200	15.2	120	9.80	1.31
4	0.5	0.200	18.8	150	5.51	2.72
4	0.5	0.201	19.8	160	5.51	2.96
4	22	0.200	22.3	180	5.51	0.70
4	22	0.201	19.5	160	5.51	0.83
5	0.25	0.200	18.3	140	3.98	2.12
5	0.25	0.200	20.7	160	3.97	2.04
5	0.5	0.200	17.4	140	3.98	1.95
5	0.5	0.200	19.8	160	3.98	1.88
5	22	0.200	18.5	150	3.98	0.57
5	22	0.199	11.7	93	3.98	0.77
6	0.5	0.180	18.4	160	9.08	5.00
7	0.5	0.180	20.1	180	9.42	5.08
7	0.5	0.180	22.2	195	9.42	5.00
7	0.5	0.180	21.5	190	9.42	5.00

TABLE 8

Isomerization of Methylnaphthalene

Number of passes	Setting point of the catalyzate	
	experiment with α-isomer	experiment with β-isomer
1	—	25°
2	—15°	20.7
3	—	16.0
4	— 9	13.5—14.2.
5	—	10.3
6	1	9—10
7	—	8.8
8	2.8	7.0
9	—	6.0
10	3.5	5.7
11	—	—
12	4.2	—

TABLE 7

Hydrogen-Exchange Experiments with β-Deuteronaphthalene After Heating Over SiO_2

Preparation No.	t_1	P_B	P_p	M	C_B^0	C_B
8	0.5	0.200	18.5	150	7.28	3.57
8	0.5	0.200	19.9	160	7.28	3.57
8	2	0.200	19.9	160	7.28	2.92
8	22	0.200	20.8	165	7.28	1.41
9	0.5	1.180	12.7	120	8.55	4.54
9	0.5	0.179	16.0	140	8.55	4.60
10	0.5	0.181	12.2	110	8.73	4.73
10	0.5	0.180	13.0	115	8.73	4.73
10	0.5	0.180	13.4	120	8.73	4.65

At the end of the experiment with the α-isomer, 2.4 g substance was obtained; with the β-isomer, 3.7 g was obtained.

In the experiment with α-methylnaphthalene the setting temperature of the catalyzate was raised with increasing number of passes; with β-methylnaphthalene the opposite effect occurred. This indicates that reciprocal transformation takes place when the vapors of the isomeric methylnaphthalenes are passed over heated silica gel.

SUMMARY

1. Experiments on hydrogen exchange between liquid hydrogen bromide and α- and β-deuteronaphthalenes enabled the velocity constants of exchange at 25° for α-deuteronaphthalene ($k = 2\text{-}3 \cdot 10^{-3}\ sec^{-1}$) and β-deuteronaphthalene ($k = 5 \cdot 10^{-5}\ sec^{-1}$) to be determined.

2. Passage of the vapors of α- and β-deuteronaphthalenes over silica gel at 420° in a nitrogen stream leads to migration of deuterium. A mixture containing approximately equal parts of both isomers is formed. Under these conditions the methyl group in methylnaphthalene likewise migrates not only from the α- into the β-position but also from the β- into the α-position.

3. No migration of deuterium in the naphthalene molecule takes place when α- and β-deuteronaphthalenes are heated for 52 hours at 400° in the absence of a catalyst.

LITERATURE CITED

[1] V. Merz and W. Weith, Ber. 3, 195 (1870).

[2] F. Mayer and R. Schiffner, Ber. 67, 67 (1934); B. G. Gavrilov and E. N. Nikitina, J. Gen. Chem. 24, 303 (1954) (T.p. 305)*; N. N. Vorozhtsov, Jr. and A. M. Beskin, J. Gen. Chem. 24, 657 (1954) (T.p. 667)*; N. N. Vorozhtsov, Jr. and N. M. Przhiyalgovskaya, J. Gen. Chem. 24, 1787 (1954) (T.p. 1755).*

[3] N. N. Vorozhtsov and N. M. Przhiyalgovskaya, J. Gen. Chem. 24, 1961 (1954) (T.p. 1929).*

[4] R. S. Urner and F. W. Bergstrom, J. Am. Chem. Soc. 67, 2108 (1945).

[5] H. Gilman, N. N. Crounse, S. P. Massie, R. A. Benkeser and S. M. Spatz, J. Am. Chem. Soc. 67, 2106 (1945).

[6] O. Kym, J. prakt. Chem. (2), 51, 325 (1894).

[7] A. I. Korolev, Bull. Acad. Sci. USSR, Div. Tech. Sci. 1938, No. 5, 95.

[8] J. D. Roberts, H. E. Simmons, L. A. Carlsmith and C. W. Vaughan, J. Am. Chem. Soc. 75, 3290 (1953).

[9] J. F. Bunnett and R. E. Zahler, Chem. Revs. 49, 273 (1951).

[10] G. Wittig, L. Pohmer, Z. angew. Chem. 67, 348 (1955).

[11] A. I. Brodsky and I. I. Kukhtenko, Proc. Acad. Sci. USSR 86, 733 (1952); Symposium: Problems of the Mechanism of Organic Reactions (Kiev, 1953), 194.

[12] V. R. Kalinachenko et al., Proc. Acad. Sci. USSR 91, 577 (1953).

[13] J. Goubeau, H. Luher, K. Feldman and G. Brandes, Ber. 86, 214 (1953).

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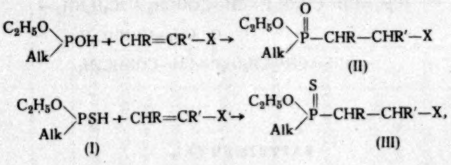
A NEW METHOD OF SYNTHESIS OF ESTERS OF PHOSPHINIC AND THIOPHOSPHINIC ACIDS

XXV. ADDITION OF MIXED DIALKYLPHOSPHOROUS AND DIALKYLTHIOPHOSPHOROUS ACIDS AND OF DIALLYLPHOSPHOROUS ACID TO UNSATURATED COMPOUNDS

A. N. Pudovik and N. I. Khlyupina

In previous communications we described the addition of dialkylphosphorous and dialkylthiophosphorous acids to unsaturated esters of carboxylic acids, unsaturated nitriles, ketones, aldehydes, imines, esters of vinyl alcohol and esters of isocyanic acid [1]. In the further development and broadening of these investigations, we have studied the addition of mixed dialkylphosphorous and dialkylthiophosphorous acids to unsaturated compounds.

Mixed dialkylphosphorous acids, as shown by B. A. Arbuzov and V. S. Vinogradova [2], are readily prepared by the transesterification reaction, by heating a dialkylphosphorous acid with the calculated quantity of alcohol in presence of phosphoric acid. Kosolapoff [3] carried out similar esterifications in the absence of catalysts. For the synthesis of mixed dialkylthiophosphorous acids we had to slightly modify the procedure suggested by the preceding authors because the transesterification of dialkylthiophosphorous acids proceeds with very much greater difficulty than that of dialkylphosphorous acids. The reactions evidently go very slowly when mixtures of diethylthiophosphorous acid and various alcohols are heated on a water bath (both in the presence and absence of phosphoric acid); the original substances are substantially recovered in spite of prolonged heating. Satisfactory results were obtained by heating the reaction mixtures in presence of a few drops of phosphoric acid for 2-3 hours at 150-165°. Yields of ethyl-alkylthiophosphorous acids were 32-39%. The constants of the synthesized ethylbutyl-, ethyl-isobutyl- and ethyl-isoamylthiophosphorous acids are presented in Table 1. Addition of mixed dialkylphosphorous and dialkylthiophosphorous acids to esters of methacrylic, cinnamic and maleic acids, methacrylonitrile, mesityl oxide and some anils was effected. The reactions were performed by the general method in presence of sodium ethoxide and may be represented by the following schemes:



$$\substack{C_2H_5O\\ Alk}{>}POH + CHR{=}CR'{-}X \rightarrow \substack{C_2H_5O\\ Alk}{>}\overset{O}{\overset{\|}{P}}{-}CHR{-}CHR'{-}X \qquad (II)$$

$$\underset{(I)}{\substack{C_2H_5O\\ Alk}{>}PSH} + CHR{=}CR'{-}X \rightarrow \substack{C_2H_5O\\ Alk}{>}\overset{S}{\overset{\|}{P}}{-}CHR{-}CHR'{-}X, \qquad (III)$$

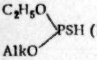
where R and R' are different alkyl and aryl radicals, and X = CN, COOR', $COCH_3$.

The constants and yields of the synthesized addition products are given in Table 2.

The only acid esters of phosphorous acids with unsaturated radicals known at the present time are those of diallylphosphorous acid which were obtained by Kamai and Shugurova [4]. Our experiments on the synthesis of dicrotylphosphorous and diisobutenylphosphorous acids were unsuccessful. Action of phosphorus trichloride on crotyl alcohol and methylvinyl carbinol gives a mixture of isomeric chlorobutenes and phosphorous acid. As was observed by Kamai and Shugurova, the process of distillation of the diallylphosphorous acid terminates with violent explosion. We also observed this. Our experiments showed, however, that the distillation can be cut short before the stage of explosion by carrying out the reaction with well-dried allyl alcohol and gradual heating of the reaction mixture after distillation of about two-thirds of the liquid. The yield of diallylpnosphorous acid is only slightly reduced by this procedure.

TABLE 1

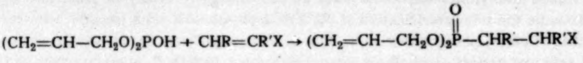
Mixed Ethyl-Alkylthiophosphorous Acids



$$(C_2H_5O)(AlkO)PSH \quad (I)$$

Acids		Yield (%)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Phosphorus content (%)	
Name	Values of Alk in formula (I)					Found	Calculated	Found	Calculated
Ethyl-n-butylthiophosphorous acid	$n\text{-}C_4H_9$	32	72-73° (3)	1.4640	1.0325	48.64	48.26	17.12	17.03
Ethyl-isobutylthiophosphorous acid	$iso\text{-}C_4H_9$	31.5	70-72 (5)	1.4565	1.0287	48.16	48.26	17.23	17.03
Ethyl-isoamylthiophosphorous acid	$iso\text{-}C_5H_{11}$	38.7	91.5-92.5 (5)	1.4480	1.0032	52.32	52.88	15.74	15.81

Addition of diallylphosphorous acid to unsaturated electrophilic reactants in presence of an alkaline catalyst goes just as easily as the addition of dialkylphosphorous acids:

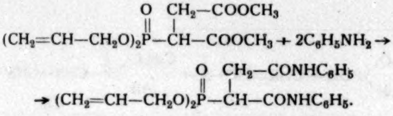


$$(CH_2{=}CH{-}CH_2O)_2POH + CHR{=}CR'X \rightarrow (CH_2{=}CH{-}CH_2O)_2\overset{\overset{\displaystyle O}{\|}}{P}{-}CHR{-}CHR'X \qquad (IV)$$

The values of R, R' and X are the same as in the preceding equations.

The constants of the synthesized products are presented in Table 3.

Heating of the dimethyl ester of diallylphosphonomaleic acid with aniline at 180-200° gave the di-(phenylamide) of diallylphosphonomaleic acid:



$$(CH_2{=}CH{-}CH_2O)_2\overset{\overset{\displaystyle O}{\|}}{P}{-}\underset{}{\overset{\overset{\displaystyle CH_2{-}COOCH_3}{|}}{C}}H{-}COOCH_3 + 2C_6H_5NH_2 \rightarrow$$

$$\rightarrow (CH_2{=}CH{-}CH_2O)_2\overset{\overset{\displaystyle O}{\|}}{P}{-}\overset{\overset{\displaystyle CH_2{-}CONHC_6H_5}{|}}{C}H{-}CONHC_6H_5.$$

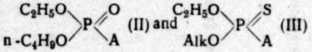
EXPERIMENTAL

Synthesis of mixed dialkylthiophosphorous acids. Mixed esters were synthesized by adding 1.5-2.5 moles alcohol and a few drops of phosphoric acid to 1 mole diethylphosphorous acid. The reaction mixtures were heated in a round-bottomed flask with a reflux condenser on an oil bath at 150-165° for 2 hours. After sucking off the hydrogen chloride and distilling off the excess of alcohol, the mixtures were distilled in vacuum.

Addition of mixed dialkylphosphorous and dialkylthiophosphorous acids and of diallylphosphorous acid to unsaturated compounds. A solution of sodium ethoxide in ethyl alcohol was slowly added dropwise to a mixture of 8-10 g unsaturated compound and an equimolar amount of the acid. An induction period is observed at first, whose

TABLE 2

Products of Addition of Ethyl-n-Butylphosphorous and Ethyl-Alklythiophosphorous Acids to the Unsaturated Compounds



$$(C_2H_5O)(n\text{-}C_4H_9O)P(=O)A \ \text{(II) and} \ (C_2H_5O)(AlkO)P(=S)A \ \text{(III)}$$

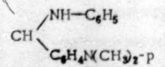
Name	Substances Value of A in formulas (II) and (III)	Yield (%)	B.p., pressure (mm)	n_D^{20}	d_4^{20}	MR_D Found	MR_D Calculated	Phosphorus content (%) Found	Phosphorus content (%) Calculated
Products of addition of ethyl-n-butylphosphorous acid (II)									
n-Butyl ester of β-(ethyl-n-butylphosphono)-α-methylpropionic acid	$CH_2CH(CH_3)COOC_4H_9$	69.3	156-158° (10)	1.4335	1.0124	79.20	79.37	10.30	10.07
Ethyl ester of β-(ethyl-n-butylphosphono)-β-phenylpropionic acid	$CH(C_6H_5)CH_2COOC_2H_5$	54.1	177-178 (8)	1.4867	1.0974	89.58	89.62	9.50	9.06
Dimethyl ester of (ethyl-n-butylphosphono)-maleic acid	$CH(COOCH_3)CH_2COOCH_3$	55.0	178-178.5	1.4405	1.1435	71.52	71.79	10.16	10.00
β-(Ethyl-n-butylphosphono)-α-methylpropionitrile	$CH_2CH(CH_3)CN$	59.7	170 (10)	1.4450	1.0577	58.63	59.00	13.27	13.30
4-Methyl-4-(ethyl-n-butylphosphono)-pentanone-2	$C(CH_3)_2CH_2COCH_3$	80.6	135-136 (10)	1.4390	1.0145	68.62	68.49	11.88	11.74
N-[m-Nitrophenyl-(ethyl-n-butylphosphono)-methyl]-m-toluidine	$CH(C_6H_4NO_2\text{-}m)NHC_6H_4CH_3\text{-}m$	49.1	M.p. 122°	—	—	—	—	7.41	7.63
N-[p-Dimethylaminophenyl-(ethyl-n-butylphosphono)-methyl]-aniline	 $CH(NH\text{—}C_6H_5)(C_6H_4N(CH_3)_2\text{-}p)$	45.6	M.p. 96°	—	—	—	—	7.76	7.93
Products of addition of ethyl-n-butyl- and ethyl-isoamlythiophosphorous acid (III)									
n-Butyl ester of β-(ethyl-n-butylthiophosphono)-α-methylpropionic acid	$CH_2CH(CH_3)COOC_4H_9\text{-}n$	70.6	146° (10)	1.4635	1.0362	86.24	86.86	9.66	9.60
β-(Ethyl-n-butylthiophosphono)-α-methylpropionitrile	$CH_2CH(CH_3)CN$	57.3	176 (10)	1.4350	0.9767	66.07	66.50	12.27	12.45
4-Methyl-4-(ethyl-isoamlythiophosphono)-pentanone-2	$C(CH_3)_2CH_2COCH_3$	79.2	153-154 (10)	1.4610	0.9977	80.87	80.60	10.87	10.55

TABLE 3

Products of Addition of Diallylphosphorous Acid to Unsaturated Compounds $CH_2{=}CH{-}CH_2O)_2P\overset{O}{\lessdot}{-}A$ (IV)

Substances		Yield (%)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Phosphorus content %	
Name	Value of A in formula (IV)					found	calculated	found	calculated
Methyl ester of β-(diallylphosphono)-α-methylpropionic acid	$CH_2CH(CH_3)COOCH_3$	67.3	143—144° (8)	1.4395	1.0753	64.16	64.58	11.73	11.83
n-Butyl ester of β-(diallylphosphono)-α-methylpropionic acid	$CH_2CH(CH_3)COOC_4H_9$-n.	65.0	176—177 (8)	1.4582	1.0573	78.50	78.44	10.14	10.19
Ethyl ester of β-(diallylphosphono)-β-phenylpropionic acid	$CH(C_6H_5)CH_2COOC_2H_5$	67.3	201—201.5 (8)	1.4960	1.1180	88.31	88.69	9.3	9.17
Dimethyl ester of (diallylphosphono)-maleic acid	$CH(COOCH_3)CH_2COOCH_3$	62.3	185 (8)	1.4300	1.1120	71.09	70.86	10.09	10.13
N-[m-Nitrophenyl-(diallylphosphono)-methyl]-m-toluidine	$CH\Big\langle\begin{matrix}C^{6}H_{4}NO_{2}\text{-}\\ NHC_6H_4CH_3\text{-}\end{matrix}$	53.7	—	—	—	—	—	7.5	7.71
N-[p-Dimethylaminophenyl-(diallylphosphono)-methyl]-aniline	$CH\Big\langle\begin{matrix}NHC_6H_5\\ C_6H_4N(CH_3)_2\text{-}\end{matrix}$	59.5	—	—	—	—	—	8.06	8.03

duration is different for each reaction. After this, the reaction goes very quickly and is accompanied by considerable heat development. The alkoxide is added until the addition no longer causes a rise of temperature of the reaction mixture. Resinification occurs in some cases when the reaction is very violent; the process is then conducted in alcohol solution. The reaction mixtures were heated for 0.5 hour on a water bath and then distilled in vacuum.

Preparation of the anilide of diallylphosphonomaleic acid. 2 g of the dimethyl ester of diallylphosphonomaleic acid and 1.2 g freshly distilled aniline were heated on an oil bath at 180-200° for 10 minutes. The crystals formed had m. p. 198° after recrystallization from alcohol.

Found %: P 7.01. $C_{22}H_{25}O_5PN_2$. Calculated %: P 7.24.

SUMMARY

1. Mixed esters of the following dialkylthiophosphorous acids were synthesized with the help of the transesterification reaction: ethyl-butyl-, ethyl-isobutyl- and ethyl-isoamylthiophosphorous acids.

2. Addition reactions were effected between ethylbutylphosphorous acid, mixed dialkylthiophosphorous acids and diallylphosphorous acid on the one hand and esters of methacrylic, cinnamic and maleic acids, and methacrylonitrile, mesityl oxide and some anils on the other hand.

LITERATURE CITED

[1] A. N. Pudovik, Progr. Chem. 22, 547 (1954).

[2] B. A. Arbuzov and V. S. Vinogradova, Proc. Acad. Sci. USSR 83, 79 (1952).

[3] G. M. Kosolapoff, J. Am. Chem. Soc. 73, 4989 (1951).

[4] G. Kh. Kamai and E. I. Shugurova, Proc. Acad. Sci. USSR 72, 301 (1950).

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SYNTHESIS OF ACYL DERIVATIVES OF O,O-DIALKYLTHIOPHOSPHATES

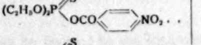
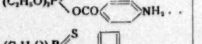
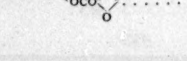
N. I. Zemlyansky and M. S. Malinovsky

Little is known about compounds with the general formula $(RO)_2P\!<\!\genfrac{}{}{0pt}{}{S}{\text{Acyl}}$, in which Acyl is the residue of an organic acid.

Only one compound of this type is described in the literature: O,O-diethyl acetylthiophosphate, prepared by Schrader [1]. In this connection we may point out that for the preparation of acyl derivatives of O,O-dialkylthiophosphate and of dialkyl phosphate, we can use not only inorganic but also organic acids, including those of the aliphatic, aromatic and heterocyclic series, as well as substituted derivatives of these acids with such substituents as halogens and the amino, nitro and other groups. The acyl derivatives are also interesting from the standpoint of their possible practical application. We therefore set out to synthesize acyl derivatives of O,O-diethylthiophosphate, containing residues of organic acids and their derivatives, by heating O,O-diethylchlorothiophosphate with salts of the respective acids in a medium of anhydrous alcohol or benzene. In some cases the reaction went better between the free acid and O,O-diethylchlorothiophosphate in presence of pyridine.

The acyl-O,O-diethylthiophosphates that we prepared are solid crystalline substances. The simplest members have fairly good solubility in water and are slowly hydrolyzed by it. The more complex members are insoluble in water. The majority have good solubility in organic solvents. All the compounds are stable in the air; many of them decompose without melting. The acyl-O,O-diethylthiophosphates that we synthesized are given in the table.

Acyl-O,O-diethylthiophosphates

Preparation No.	Formula of compound	Melting point	Yield (%)	analytical data: found/calc. S (%)	P (%)	M
1	$(C_2H_5O)_2P\!<\!\genfrac{}{}{0pt}{}{S}{OCOCH_3}$	64°	29.2	$\frac{14.69}{15.10}$	$\frac{14.02}{14.56}$	$\frac{198}{205}$
2	$(C_2H_5O)_2P\!<\!\genfrac{}{}{0pt}{}{S}{OCOCH_2Cl}$	200(with decomp)	12.0	$\frac{12.75}{13.00}$	$\frac{11.87}{12.52}$	$\frac{235}{235}$
3	$(C_2H_5O)_2P\!<\!\genfrac{}{}{0pt}{}{S}{OCOCCl_3}$	Decomposes at 19 —200	16.0	$\frac{10.04}{10.16}$	$\frac{8.58}{8.58}$	$\frac{292}{315.5}$
4	$(C_2H_5O)_2P\!<\!\genfrac{}{}{0pt}{}{S}{OCOCH_2NH_2}$	115	14.6	$\frac{13.79}{41.11}$	$\frac{13.50}{13.62}$	$\frac{237}{227}$
5	$(C_2H_5O)_2P\!<\!\genfrac{}{}{0pt}{}{S}{OCOC_6H_5}$	111—112	55.5	$\frac{11.21}{12.04}$	$\frac{10.61}{11.32}$	$\frac{261.7}{274.1}$
6		234—235	13.1	$\frac{9.12}{10.03}$	$\frac{8.86}{9.72}$	$\frac{306.2}{319.15}$
7		148—150	14.0	$\frac{10.26}{11.08}$	$\frac{10.11}{10.73}$	$\frac{276.1}{289.15}$
8		Decomposes	4.0	$\frac{11.70}{12.11}$	$\frac{11.04}{11.70}$	$\frac{251}{264}$

EXPERIMENTAL

Synthesis of acyl derivatives. 0.03 mole O,O-diethylchlorothiophosphate, 0.03 mole anhydrous, thoroughly pulverized sodium acetate and 30 ml anhydrous alcohol were charged into a flask with a reflux condenser closed with a calcium chloride tube. The mixture was boiled on water bath, while stirring, for 1 hour. The alcoholic solution was filtered from the precipitate and the alcohol was distilled off from the filtrate. The residue was the corresponding O,O-diethylthiophosphate, which was purified by recrystallization from alcohol. Compounds 1-4 listed in the table were prepared by this method.

Compound 5 was obtained in a benzene medium by dropwise introduction of O,O-diethylchlorothiophosphate to a triple excess of sodium benzoate suspended in benzene, with mechanical stirring.

Compounds 6 and 7 were obtained by heating a mixture of O,O-diethylchlorothiophosphate with a 50% excess of the acid component (p-nitrobenzoic or p-aminobenzoic acid) in presence of pyridine and benzene as solvents.

Compound 8 was prepared in a chlorobenzene medium in presence of a few drops of pyridine [2].

SUMMARY

1. The possibility of preparing mixed anhydrides of O,O-diethylthiophosphoric acid and organic acids by heating O,O-diethylchlorothiophsophate with salts of organic acids was demonstrated. In some cases the free acids were used, and the reaction was conducted in presence of pyridine.

2. Using the above methods, the following were prepared for the first time: chloroacetyl-O,O-diethylthiophosphate; trichloro-O,O-diethylthiophosphate; aminoacetyl-O,O-diethylthiophosphate; benzoyl-O,O-diethylthiophosphate; p-nitrobenzoyl-O,O-diethylthiophosphate; p-aminobenzoyl-O,O-diethylthiophosphate; and the anhydride of pyromucic and O,O-diethylthiophosphoric acids. All the compounds are crystalline solids.

LITERATURE CITED

[1] G. Schrader, Progr. Chem. 22, 754 (1953).

[2] A. Toy and T. Beck, J. Am. Chem. Soc. 72, 3191 (1950).

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Lvov State University

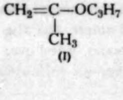
THE POLYMERIZATION OF α-METHYLVINYL ALKYL ETHERS

III. POLYMERIZATION OF α-METHYLVINYL PROPYL AND BUTYL ETHERS

M. F. Shostakovsky and E. P. Gracheva

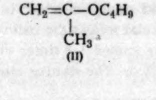
The α-substituted unsaturated ethers [1] of general structure: $CH_2=\underset{\displaystyle R}{\underset{|}{C}}-OR$, where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_5 are important members of the large number of vinyl ethers known. As is known, the double bond in vinyl alkyl ethers [2] is highly nucleophilic, which property is very clearly manifested in the various ionic transformations shown by these compounds.

In this communication we discuss the reactivity shown by α-methylvinyl propyl (I) and α-methylvinyl butyl (II) ethers in their ionic reactions:



$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-OC_3H_7$$

(I)



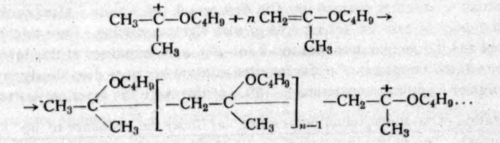
$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-OC_4H_9$$

(II)

We described the synthesis, hydrolysis and acetal formation of these compounds in previous communications [3]. In this paper we will discuss their polymerization and copolymerization with various vinyl alkyl ethers, proceeding under the influence of ionic catalysts.

The ethers (I, II) were polymerized in the presence of either $FeCl_3$ or BF_3 as the catalyst, taken in either alcohol or dioxane solution. We postulate that the indicated catalysts have the following structure in the first reaction stage: $(FeCl_3 \cdot OH)^- + H^+$ and $(BF_3 \cdot OH)^- + H^+$.

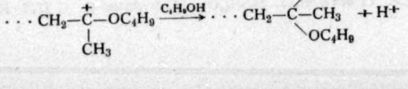
The proton then manifests its further action in carbonium ion formation, which ion is responsible for the ionic course of the polymerization reaction, proceeding by the scheme



$$CH_3-\overset{+}{\underset{\displaystyle CH_3}{\underset{|}{C}}}-OC_4H_9 + n\,CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-OC_4H_9 \rightarrow$$

$$\rightarrow CH_3-C(OC_4H_9)(CH_3)\left[-CH_2-C(OC_4H_9)(CH_3)\right]_{n-1}-CH_2-\overset{+}{\underset{\displaystyle CH_3}{\underset{|}{C}}}-OC_4H_9\ldots$$

The last link can be formed by the following schemes:



$$\cdots CH_2-\overset{+}{\underset{\displaystyle CH_3}{\underset{|}{C}}}-OC_4H_9 \xrightarrow{C_4H_9OH} \cdots CH_2-C(OC_4H_9)_2-CH_3 + H^+ \qquad (1)$$

(2)

In our study we found that compounds I and II show a greater polymerization tendency than do the vinyl alkyl ethers $CH_2 = CHOR$. This appears first of all in the fact that the polymerization of ethers I and II proceeds at a lower temperature than is true for the corresponding vinyl alkyl ethers [4]. The temperature conditions for the polymerization of compounds I and II under the influence of the indicated catalysts lie in the negative temperature region (from -15 to -20°) while the vinyl alkyl ethers of the same alcohols $CH_2 = CHOC_3H_7(C_4H_9)$(III) are polymerized at their boiling points [5]. We consider such a difference in the polymerization conditions, for example, of the vinyl butyl and α-methylvinyl butyl ethers, to lie in the different stability shown by the oxonium compounds, formed here by the reaction of the ionic catalysts with ether oxygen.

We next compared the reactivity of the α-methylvinyl butyl and vinyl butyl ethers by studying their mutual copolymerization. When an attempt was made to copolymerize the α-methylvinyl butyl ether with vinyl butyl ether under the optimum polymerization conditions for either, it was found that, depending on the polymerization temperature used, the polymer contained only one of the ethers present in the original mixture. As regards the reactivity shown by ethers I and II in radical reactions, it is our opinion that it is lowered. For example, we were unable to realize their polymerization under the influence of an initiator capable of evoking free radical reactions (isobutyric acid, 2,2-bisazonitrile [6]). The conditions used to polymerize the indicated unsaturated ethers and the properties of the obtained polymers are described in the experimental section.

EXPERIMENTAL

The substituted vinyl ethers were synthesized by the A. E. Favorsky and M. F. Shostakovsky method, starting from the corresponding alcohols and methylacetylene in the presence of potassium hydroxide [3]. In order to obtain polymers with a higher molecular weight, the indicated ethers and also the vinyl butyl ether were well purified. Therefore each crude ether was washed 7-8 times with water, dried over fused potash, let stand over metallic sodium for several hours, and distilled. The starting ethers had the following constants:

α-Methylvinyl butyl ether: B.p. 111.5-112° (751 mm), n_D^{20} 1.4111, d_4^{20} 0.7955; α-methylvinyl propyl ether: B.p. 78.5° (756 mm), n_D^{20} 1.3990, d_4^{20} 0.7861; vinyl n-butyl ether: B.p. 93-94°, n_D^{20} 1.4030, d_4^{20} 0.7793.

The obtained polymers were isolated in pure form by dissolving them in either diethyl ether or acetone, and precipitating them with methyl alcohol from the indicated solutions. Then most of the solvent and methyl alcohol was removed by decantation and the precipitated polymer was heated in vacuo for 4-5 hours at 50-60° and 20 mm to constant weight. The viscosity determinations (in centipoises) were run at 20° in an Ostwald viscosimeter, using solutions containing 1 g of polymer in 100 ml of benzene.

A three-necked flask, fitted with stirrer, reflux condenser and thermometer, was used to polymerize the α-methylvinyl alkyl ethers under the influence of either 5% $FeCl_3$ or BF_3 solution in either dioxane or alcohol. The amount of unsaturated α-ether charged into the flask was 0.1-0.2 mole. After cooling to -15 to -17°, to the ether was added 3 drops of catalyst (about 0.03 g) with vigorous stirring. Here thickening of the reaction mixture was observed and the temperature rose to -7 to -8°, and remained at this level for 1-1.5 hours in spite of cooling. After this, the temperature of the reaction mixture began to drop slowly, and in approximately an hour assumed the original reaction temperature (-15°). At this stage the reaction was terminated.

1. Polymerization of α-methylvinyl butyl ether. a) Under the influence of 5% $FeCl_3$ solution in either dioxane or ethyl alcohol. The polymerization of 11.2 g of the ether in the presence of 3 drops of $FeCl_3$ solution in dioxane (or ethyl alcohol) gave 10.6 g (95%) of light yellow viscous polymer. The purified product had the following constants:

n_D^{20} 1.4599; 1.4642, d_4^{20} 0.9426; η_{20} 0.9760, 0.9769 (in centipoises).
Found %: C 73.8; H 12.5. M 5817, 6111. $(C_7H_{14}O)_n$. Calculated %: C 73.7; H 12.4.

When the polymer is heated at 80-100° for 2-3 hours, its viscosity drops to 0.6712 centipoises. Evidently destruction of the polymer occurs here.

b) Under the influence of 5% BF$_3$ solution in either dioxane or ethyl alcohol. The polymerization of 11.2 g of α-methylvinyl butyl ether in the presence of three drops of BF$_3$ solution in dioxane (or ethyl alcohol) gave 10.8 g (97%) of a slightly yellowish viscous polymer, which after purification had viscosity η_{20} 0.9760, 0.09762 (in centipoises).

Found %: C 73.75; H 12.6. M 5962, 6003. $(C_7H_{14}O)_n$. Calculated %: C 73.7; H 12.4.

2. Polymerization of α-methylvinyl propyl ether. a) Under the influence of 5% FeCl$_3$ solution in either dioxane or ethyl alcohol. For reaction was taken 20 g of the ether and 3 drops of FeCl$_3$ solution in dioxane (or ethyl alcohol). The polymerization gave 19.4 g (97%) of a light yellow viscous polymer, which after purification had: n_D^{20} 1.4577, 1.4605; d_4^{20} 0.9403; η_{20} 0.9602, 0.9587 (in centipoises).

Found %: C 71.78, 71.81; H 11.82, 12.01. M 5772, 6802. $(C_6H_{12}O)_n$. Calculated %: C 72.00; H 12.00.

b) Under the influence of 5% BF$_3$ solution in either dioxane or ethyl alcohol. The polymerization of 20 g of the ether in the presence of BF$_3$ in dioxane (or ethyl alcohol) gave 19.8 g (99%) of a slightly yellowish polymer, which after purification had viscosity η_{20} 0.9583, 0.9591 (in centipoises).

Found%: C 71.83; H 11.81. M 5803, 5826. $(C_6H_{12}O)_n$. Calculated %: C 72.00; H 12.00.

3. Polymerization of α-methylvinyl butyl ether under the influence of isobutyric acid 2,2-bisazonitrile. A mixture of 20 g of the α-ether and 0.1 g of crystalline catalyst was placed in a sealed ampoule and heated without interruption for 150 hours in a thermostat at 60°. We recovered 19.6 g (98%) of the α-ether taken, and here the catalyst had crystallized on the sides of the flask. The same results were obtained when the catalyst amount was increased to 0.5 and to 1 g.

4. Copolymerization of α-methylvinyl butyl ether with vinyl butyl ether under the influence of 6%* FeCl$_3$ solution in dioxane. a) Copolymerization at 94 and 112° (boiling points of the ethers). Into a three-necked flask, fitted with mechanical stirrer, thermometer, dropping funnel and reflux condenser, was charged a mixture of 20 g of vinyl butyl ether and 22.8 g of α-methylvinyl butyl ether. The mixture was heated to 94° (boiling point of vinyl butyl ether). To the boiling mixture was added 3 drops of 5% FeCl$_3$ solution in dioxane. The mixture congealed rapidly. Vacuum-distillation gave 22.2 g of product with b.p. 56° at 38 mm (111-112° at 751 mm), n_D^{20} 1.4112, from the constants corresponding to α-methylvinyl butyl ether. The residue in the flask (19.6 g) was a viscous light yellow product, after purification having n_D^{20} 1.4575, d_4^{20} 0.9335, η_{20} 0.8990 (centipoises), which corresponds to the polymer of vinyl butyl ether [4].

Copolymerization of the indicated ethers at 112° (boiling point of α-methylvinyl butyl ether) gave analogous results.

b) Copolymerization at -15 to -17°. In a small three-necked flask, fitted with mechanical stirrer, thermometer, dropping funnel and reflux condenser, was placed 20 g of vinyl butyl ether and 22.8 g of α-methylvinyl butyl ether. The mixture was cooled to -17°. To the cooled mixture was added 3 drops of 5% FeCl$_3$ solution in dioxane. Within several seconds the reaction mass rapidly congealed and the temperature rose to -5° to -7°. Vacuum distillation into a coil receiver cooled in a Dewar vessel gave 19.6 g of product with b.p. 49° at 36 mm (93-94° at 751 mm), n_D^{20} 1.4015, from the constants corresponding to the starting vinyl butyl ether. The light yellow viscous product (21.9 g) remaining in the flask after purification had n_D^{20} 1.4642, η_{20} 0.9762 (centipoises), which coincide with the constants obtained for the polymer of α-methylvinyl butyl ether.

Found %: C 73.6; H 12.4. $(C_7H_{14}O)_n$. Calculated %: C 73.7; H 12.4.

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*As in original - Publisher.

SUMMARY

1. Conditions were established for the ionic polymerization of α-methylvinyl propyl and butyl ethers with $FeCl_3$ and BF_3 catalysts in either dioxane or alcohol solution. The obtained polymers were characterized.

2. It was shown that the polymerization of α-methylvinyl butyl ether does not proceed in the presence of a radical catalyst (isobutyric acid 2,2-bisazonitrile).

3. An attempt to copolymerize α-methylvinyl butyl ether with vinyl butyl ether under the influence of the ionic catalysts $FeCl_3$ and BF_3 in either dioxane or alcohol solution proved unsuccessful.

4. The increased ionic reactivity shown by α-vinyl alkyl ethers was demonstrated.

LITERATURE CITED

[1] M. F. Shostakovsky and E. P. Gracheva, J. Gen. Chem. 23, 1153 (1953) (T.p. 1209).*

[2] M. F. Shostakovsky, Simple Vinyl Ethers (Acad. Sci. USSR Press, 1952), 216.

[3] M. F. Shostakovsky and E. P. Gracheva, J. Gen. Chem. 23, 1320 (1953) (T.p. 1383).*

[4] M. F. Shostakovsky, J. Gen. Chem. 13, 180, 674 (1943); M. F. Shostakovsky and V. A. Gladyshevskaya, Bull. Acad. Sci. USSR 1953, 351 (T.p. 319).*

[5] M. F. Shostakovsky, P. V. Deryagin and P. F. Bogdanov, J. Appl. Chem. 24, 1063 (1951) (T.p. 1209).*

[6] M. F. Shostakovsky and A. V. Bogdanova, Bull. Acad. Sci. USSR 1954, 911 (T.p. 789).*

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FREE RADICAL REACTIONS OF LEAD TETRAACETATE

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Although a large number of papers have been devoted to a study of the reactions shown by lead tetraacetate, up to the present time there does not exist a single opinion as to the mechanism of these reactions. Only the fact that $Pb(OCOCH_3)_4$ can react in two directions is without doubt: it can react in either an ionic or radical sense. Thus, for example, the decomposition of the tetraacetate in acetic acid [1] proceeds with the participation of $CH_3COO\cdot$, $\cdot Pb(OCOCH_3)_3$, $\cdot CH_2COOH$ and $CH_3\cdot$. Here it is assumed that the initial stage consists in the decomposition of $Pb(OCOCH_3)_4$ into lead diacetate and the radical $CH_3COO\cdot$; consequently, in its free radical reactions the tetraacetate should behave like acetyl peroxide. In studying the latter we observed that it gave characteristic reactions with metallic mercury [2], to which the $CH_3\cdot$ and $CH_3COO\cdot$ radicals became fixed with the formation of $CH_3HgOCOCH_3$ and $Hg_2(OCOCH_3)_2$, and also that it initiates the decomposition of organic acid mercury (Hg^{II}) salts [3].

It seemed of interest to us to determine if $Pb(OCOCH_3)_4$ would show similar reactions. Actually, the formation of $Hg_2(OCOCH_3)_2$ in quantitative yield was observed even when lead tetraacetate was reacted with metallic mercury in benzene medium at room temperature, and the formation proceeded more rapidly in boiling solvent. It should be mentioned that here, in contrast to the reaction of acetyl peroxide with mercury, we were unable to find $CH_3HgOCOCH_3$ among the reaction products. This fact indicates that $Pb(OCOCH_3)_4$ shows cleavage of $CH_3COO\cdot$ radicals. The fact that acetoxy radicals are formed in the decomposition of lead tetraacetate was also confirmed by the initiated decarboxylation of the latter with mercuric oxide.

When a mixture of $Hg(OCOCH_3)_2$ and $Pb(OCOCH_3)_4$ was heated in benzene under vigorous stirring, it was observed that traces of $CH_3HgOCOCH_3$ and a large amount of mercurous acetate (72% yield, based on starting mercuric acetate) were formed. If the reaction is run in glacial acetic acid, the yield of methylmercury acetate is sharply increased (82% yield, based on starting lead tetraacetate); at the same time a 24% yield (based on starting mercuric acetate) of mercurous acetate is obtained. The amount of $Hg_2(OCOCH_3)_2$ formed in the given reaction is 5.5 times the theoretical, which indicates the chain character of the process.

It should be mentioned that the reaction with acetyl peroxide also proceeds better in acetic acid medium than in benzene. Acetyl peroxide is a much stronger initiator of $Hg(OCOCH_3)_2$ decarboxylation.

We became interested in the possibility of obtaining methyl derivatives of lead by the decomposition of $Pb(OCOCH_3)_4$ as with the corresponding mercury salts. The reaction products of lead tetraacetate with acetic acid are described in detail in the literature [1], but the lead compounds that are formed here were not studied. The only assumption we made was that they represent a mixture of salts of acetic and acetoxyacetic acids. We ran some experiments on the decomposition of $Pb(OCOCH_3)_4$ in benzene and in acetic acid, where we found that the reaction is initiated either by the addition of acetyl peroxide or by the action of ultraviolet light (PRK-4 lamp). In not a single instance were we able to establish the formation of methyl lead derivatives.

EXPERIMENTAL

Reaction of lead tetraacetate with metallic mercury in benzene medium at room temperature. A mixture of 1.0 g of lead tetraacetate, 30.0 g of mercury and 25 ml of benzene was shaken on a machine in a ground-glass stoppered flask for 20 hours. After several hours the formation of a white benzene-insoluble substance was observed. On conclusion of reaction, the solvent and deposit were separated from the metallic mercury, after which the lead acetate was removed with water and precipitated with Na_2SO_4; here 0.68 g of $PbSO_4$ was obtained. The residue after removal of the $Pb(OCOCH_3)_2$ was mercurous acetate, yield 1.14 g (97.4%).

Reaction of lead tetraacetate with metallic mercury in benzene medium under heating. A mixture of 2.0 g of lead tetraacetate, 50.0 g of mercury and 100 ml of benzene was heated at the boil with mechanical stirring for 6 hours in a flask, fitted with thermometer and reflux condenser, and connected to a gas buret. Gas evolution was not observed. Further treatment of the reaction products was the same as before; here we obtained 1.27 g of $PbSO_4$ and 2.27 g of $Hg_2(OCOCH_3)_2$ (97.3% yield).

Reaction of lead tetraacetate with mercuric acetate in benzene medium. A mixture of 3.0 g of lead tetraacetate, 15.0 g of $Hg(OCOCH_3)_2$ and 100 ml of benzene was heated under stirring until gas ceased to evolve. The resulting precipitate was filtered, and the benzene filtrate was washed several times with water. On addition of saturated NaCl solution, the combined water extracts were steam-distilled. Treatment of the distillate with potassium iodide resulted in the precipitation of 0.002 g of CH_3HgI. The lead acetate (1.88 g of $PbSO_4$) was removed from the precipitate (11.58 g) by washing; the yield of $Hg_2(OCOCH_3)_2$ was 8.73 g (71.6%).

Reaction of lead tetraacetate with mercuric acetate in acetic acid medium. A mixture of 0.5 g of lead tetraacetate, 15.0 g of $Hg(OCOCH_3)_2$ and 100 ml of glacial acetic acid was heated at 121° until gas ceased to evolve. From the reaction mixture 1.1 g of mercurous acetate was removed by filtration. Treatment of the filtrate in the same manner as in the preceding experiment gave 0.63 g of methylmercury iodide (3.6% yield, based on starting mercuric acetate; 81.8%, based on lead tetraacetate). The residue from the steam distillation was calomel, weight 1.7 g. Consequently, the total yield of mercurous acetate was 24.4%. The filtrate from the Hg_2Cl_2 removal was treated with potassium iodide to give a precipitate of mixed HgI_2 and PbI_2 (14.85 g). The mercuric iodide was removed by washing with excess KI solution. The weight of PbI_2 was 0.5 g, and the weight of HgI_2 (by difference) was 14.35 g.

SUMMARY

1. Lead tetraacetate reacts with metallic mercury in benzene medium at room temperature, giving mercurous acetate in quantitative yield; the reaction proceeds more rapidly if the mixture is heated.

2. Methylmercury acetate is obtained in good yield when a mixture of lead tetraacetate and mercuric acetate is boiled in glacial acetic acid.

3. The reaction proceeds in similar manner in benzene to give mainly mercurous acetate and traces of methylmercury acetate.

4. The attempts made to isolate methyl lead derivatives from the products of lead tetraacetate reaction, initiated by either acetyl peroxide or by ultraviolet in the two solvents, proved unsuccessful.

LITERATURE CITED

[1] M S. Kharasch, H. Friedlender and W. H. Urry, J. Org. Chem. 16, 533 (1951).

[2] G. A. Razuvaev, Yu. A. Oldekop and L. N. Grobov, J. Gen. Chem. 23, 589 (1953) (T.p. 613).*

[3] G. A. Razuvaev, Yu. A. Oldekop and N. A. Maier, J. Gen. Chem. 25, 697 (1955) (T.p. 665).*

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THE CATALYTIC DECOMPOSITION OF PHENYLMERCURY HYDROXIDE IN SOLVENTS

G.A. Pazuvaev, G.G. Petukhov and R.V. Kalinina

In the studies made by G. P. Miklukhin and A. F. Rekasheva [1], it was shown that deuterium-containing benzene is formed in the reduction of diazo compounds with formaldehyde in heavy water. A change in the mechanism of this process is observed if the reaction is run in the presence of copper salts and only light benzene is obtained. We had observed earlier [2] a certain analogy in the reaction of diazo compounds and of phenylmercury hydroxide with alcohols, for which reason it seemed of interest to determine if the addition of copper salts would influence the reaction of phenylmercury hydroxide with CH_3CH_2OD. It was revealed that the addition of copper acetate strongly retards the course of the photo reaction. In view of this we had to resort to the thermal decomposition of the hydroxide into CH_3CH_2OD. In both cases, i.e. with the addition of a copper salt and without it, the isolated benzene and acetaldehyde failed to contain deuterium. On this basis the reaction can be depicted by the equation:

$$C_6H_5HgOH + CH_3CH_2OD \rightarrow C_6H_6 + Hg + HOD + CH_3CHO.$$

Analysis of the alcohol, isolated from the reaction by leaching, revealed that the deuterium of the hydroxyl group had failed to migrate into the alcohol radical.

We next ran the decomposition of phenylmercury hydroxide in benzene solution with and without the addition of copper acetate. In this solvent, as is known [3], phenylmercury hydroxide reacts under photoillumination to yield diphenyl. The reaction to yield deuterobenzene proceeded by the equation:

$$C_6H_5HgOH + C_6D_6 \rightarrow C_6H_5C_6D_5 + Hg + HOD.$$

Our thermal reaction between phenylmercury hydroxide and benzene led to the formation of insoluble polymeric compounds, the formation of which was also observed earlier in the thermal reactions of diphenylmercury [4].

$$x\,C_6H_5HgOH \rightarrow x\,H_2O + (C_6H_4Hg)_x.$$

The addition of copper acetate completely changed the course of the reaction: here mercury was liberated and phenol was isolated. Diphenyl was obtained only in very small amount. The reaction can be depicted by the equation:

$$C_6H_5HgOH \rightarrow C_6H_5OH + Hg.$$

Earlier we had completely failed to observe the formation of phenol in the reactions of phenylmercury hydroxide [2]. In the present case, evidently, the liberated copper oxide exerts a catalytic influence, which leads to decomposition of the organometallic compound (such decomposition was described [5] for the fully organometallic compounds and, evidently, the reaction also extends to the hydroxide). The hydroxide is decomposed on the catalyst surface with the liberation of mercury, while the phenyl and hydroxyl radicals combine with each other to form phenol.

It seemed of interest to determine if the exchange reaction would proceed between the formed phenyl radical and the solvent – heavy benzene in the present case:

$$C_6H_5\cdot + C_6D_6 \rightarrow C_6H_5D + C_6D_5\cdot,$$

or between the hydroxyl group and the heavy benzene:

$$HO\cdot + C_6D_6 \rightarrow HDO + C_6D_5\cdot,$$

as was the case in our earlier studied photo-reactions [3].

Therefore we ran the reaction for the catalytic formation of phenol from phenylmercury hydroxide in heavy benzene. Here, if the above indicated processes were present, the obtained phenol should have contained deuterium. However, as experiment revealed, the isolated phenol was practically devoid of deuterium. From this it can be concluded that the phenyl and hydroxyl groups, formed on the catalyst surface, react directly with each other without involving the solvent. In all cases using copper acetate, an acceleration of the hydroxide decomposition process was observed which can be explained by the reaction of copper acetate with the latter:

$$2C_6H_5HgOH + Cu(CH_3COO)_2 \rightarrow 2C_6H_5HgOCOCH_3 + H_2O + CuO.$$

EXPERIMENTAL

The thermal reactions were run by heating the reaction mixture in sealed ampoules. The starting products and the substances isolated from the reactions were analyzed for their deuterium content by the method of determining the flotation value of their combustion water. The measurement accuracy was 15-20γ.

Thermal decomposition of phenylmercury hydroxide in CH_3CH_2OD. Five grams of phenylmercury hydroxide in 15 ml of CH_3CH_2OD was heated for 151 hours at 180-185°. The amount of metallic mercury isolated from the reaction was 3.4 g (65.3%). The filtrate, containing benzene and acetaldehyde, was diluted with water. The benzene that separated here was extracted with CCl_4, and then nitrated to m-dinitrobenzene in the same solvent. The yield of m-dinitrobenzene was 1.07 g (37.6%), m.p. 89°. The acetaldehyde was isolated from the aqueous alcohol solution as the 2,4-dinitrophenylhydrazone (0.7 g, 18.4%). The residual solution was then distilled to remove the alcohol. The hydroxyl deuterium of this alcohol was leached out by repeated dilution with water and subsequent removal of the alcohol by distillation. After the latter had been made absolute, the fraction with b.p. 78° was collected. The isolated m-dinitrobenzene, 2,4-dinitrophenylhydrazone acetaldehyde, and leached alcohol were subjected to combustion, and the waters were analyzed for their deuterium content.

Thermal decomposition of phenylmercury hydroxide in CH_3CH_2OD in the presence of $Cu(CH_3COO)_2$. A mixture of 8.2 g of phenylmercury hydroxide and 0.2 g of $Cu(CH_3COO)_2$ in 15 ml of CH_3CH_2OD was heated for 131 hours at 150-155°. The reaction products [mercury (5 g, 99%), m-dinitrobenzene (1.4 g, 33.3%, m.p. 89°), acetaldehyde dimedon derivative (0.9 g) and leached alcohol] were isolated in the same manner as in the preceding experiment. In addition, 0.07 g of phenylmercury acetate and 0.1 g of CuO were isolated. The waters obtained from the combustion of the m-dinitrobenzene, acetaldehyde dimedone derivative and leached alcohol were analyzed for their deuterium content.

Thermal decomposition of phenylmercury hydroxide in benzene. Five grams of phenylmercury hydroxide in 20.4 g of benzene was heated for 217 hours at 150-160°. From the deposit were isolated metallic mercury (0.7 g) and 2.1 g of polymercury compounds, the latter being insoluble in organic solvents and not subjected to closer study. After distilling off the benzene the filtrate was worked up to give 0.5 g of phenylmercury hydroxide, m.p. 199°; its mixed melting point with the original pure substance was not depressed.

Thermal decomposition of phenylmercury hydroxide in C_6D_6 in the presence of $Cu(CH_3COO)_2$. Eight grams of phenylmercury hydroxide in 24.5 g of C_6D_6 was heated for 120 hours at 190-195° with 0.1 g of $Cu(CH_3COO)_2$. From the deposit was isolated 3 g (83.3%) of metallic mercury and 0.1 g of CuO. The benzene was removed from the filtrate by distillation. The undistilled residue was steam-distilled. Here 0.4 g of diphenyl was isolated, m.p. 69°. The aqueous distillate contained phenol, which was precipitated as tribromophenol. The yield of the latter was 0.8 g (89%), m.p. 93°. Its mixed melting point with the pure substance was not depressed. From the residue after steam distillation 0.04 g of phenylmercury acetate was isolated, m.p. 143°. The water obtained from the tribromophenol combustion was analyzed for its deuterium content.

The experimental results are given in the table.

Thermal Reactions of Phenylmercury Hydroxide in Solvents

Expt. No.	Solvent	Deuterium content in starting solvent (in γ)	Catalyst	Time of heating (in hours)	Deuterium content in in the isolated products (in γ)			
					benzene	aldehyde	phenol	leached alcohol
1	CH_3CH_2OD	5700	—	151	0	2	—	1
2	CH_3CH_2OD	5700	$Cu(CH_3COO)_2$	131	18	40	—	5
3	C_6D_6	865	$Cu(CH_3COO)_2$	120	—	—	20	—

Remarks. The deuterium content of the alcohol is shown in the hydroxyl group.

SUMMARY

1. The heating of phenylmercury hydroxide with ethanol containing deuterium in the hydroxyl group either in the presence or absence of copper salts gives benzene that is devoid of deuterium.

2. The heating of phenylmercury hydroxide in benzene solution with the addition of copper acetate yields phenol, and metallic mercury is liberated.

3. When the catalytic decomposition of phenylmercury hydroxide was run in heavy benzene we did not observe any exchange between the formed radicals and the solvent.

LITERATURE CITED

[1] G. P. Miklukhin and A. F. Rekasheva, Problems of Chemical Kinetics, Catalysis and Reactivity (Acad. Sci. USSR Press, 1955), 24.

[2] G. A. Razuvaev and G. G. Petukhov, J. Gen. Chem. 21, 646 (1951) (T.p. 713).•

[3] G. A. Razuvaev, G. G. Petukhov, A. F. Rekasheva and G. P. Miklukhin, Proc. Acad. Sci. USSR 90, 569 (1953).

[4] G. A. Razuvaev and M. M. Koton, J. Gen. Chem. 3, 496 (1933).

[5] Ibid., 792.

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•T.p. = C. B. Translation pagination.

[illegible]

The experimental results are given in the table.

Thermal [illegible] of Phenylmercury [illegible]

[illegible]	Solvent	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

Remarks. The [illegible] content of the [illegible] is [illegible].

CONCLUSIONS

1. Cleavage of phenylmercury [illegible] with [illegible] takes place [illegible] in the presence or absence of [illegible], which [illegible].

2. The [illegible] of phenylmercury [illegible] is [illegible].

3. When the catalytic [illegible] of phenylmercury [illegible] we did not observe any exchange between the [illegible] and the [illegible].

LITERATURE CITED

[1] A. N. Nesmeyanov, [illegible]

[2] O. A. Reutov and [illegible]

[3] A. N. Nesmeyanov, O. A. Reutov, [illegible]

[4] O. A. Reutov and [illegible]

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TRANSFORMATION OF TETRAETHYLSILANE ON CHROMIUM CATALYST

B.N. Dolgov, G.V. Golodnikov and N.E. Glushkova

Tetraethylsilane, showing a symmetrical structure and containing very stable ethyl radicals, is characterized by both high thermal and chemical stability. In the absence of catalysts, tetraethylsilane in a hydrogen atmosphere does not show change even at 500° [1]. At higher temperature the tetraethylsilane is pyrolyzed to yield silicon, ethylene and hydrogen [2]. The destructive hydrogenation of tetraethylsilane over activated aluminosilicate catalyst at 550° leads to the formation of triethylsilane and ethane; however, with elevation of the temperature to 600° the reaction for the thorough hydrogenolysis of tetraethylsilane to silicon and ethane begins to predominate [1].

In this paper we studied the transformations suffered by tetraethylsilane on the chromium catalyst used for the dehydrogenation and dehydrocyclization of saturated hydrocarbons. In particular, it seemed of interest to elucidate the possibility of subjecting this silicohydrocarbon to catalytic dehydrogenation.

However, our experiments revealed that the proposed reaction for the formation of triethylvinylsilane on a chromium catalyst does not occur. From the table it can be seen that tetraethylsilane begins to decompose at 510-530°. As the temperature is raised above this point the yield of triethylsilane and amount of ethylene in the gas show corresponding increase, attaining their maximum values at 600°. Consequently, in the interval 530-600° the transformation proceeds mainly in accord with the reaction:

$$Si(C_2H_5)_4 \rightarrow (C_2H_5)_3SiH + C_2H_4.$$

The reduction in the yields of condensate, the increase in the amount of paraffins in the gas, and the deposition of silicon on the catalyst, all observed at elevated temperatures (600-630°), serve as evidence that here the main reaction is accompanied by profound hydrogenolysis processes:

$$Si(C_2H_5)_4 + 2H_2 \rightarrow Si + 4C_2H_6,$$

$$(C_2H_5)_3SiH + H_2 \rightarrow Si + 3C_2H_6.$$

An increase in the contact time (reduction in the space velocity to 20) raises the degree of transformation and facilitates obtaining higher yields of triethylsilane, ethylene and ethane.

A slightly higher yield of triethylsilane was obtained when the experiment was run in the absence of hydrogen than when the same experiment (at 550°) was run with the addition of hydrogen.

The condensates obtained from all of the experiments represented binary mixtures of triethylsilane and tetraethylsilane, which when rectified gave fractions boiling at 105-120° and 140-152°. The 105-120° fraction was almost pure triethylsilane. The 140-152° fraction was mostly tetraethylsilane (b.p. 152.2°), but it could be assumed that some triethylvinylsilane (b.p. 146°) was also present. The Raman spectrum obtained by us for the 140-152° fraction shows a number of lines characteristic for the Si–C and Si–H bonds, but it does not contain any lines that correspond to the frequency characteristic for the double bond found in α-alkenylsilanes.

Temperature	Space velocity	Yield of condensate (passed tetraethylsilane, %)	Yield (passed tetraethylsilane based on anal. of the fractions, %)		Amount in the gas (volume %)			Yield of ethylene (passed tetraethylsilane based on anal. of the gas, %)	Yield of ethane (passed tetraethylsilane based on anal. of the gas, %)
			triethylsilane	unchanged tetraethylsilane	C_2H_4	H_2	C_2H_6		
500°	40	100.0	2.0	98.0	0.0	98.2	0.0	0.0	0.0
510	41	98.4	2.5	95.0	2.2	95.6	1.1	0.7	0.4
520	40	98.2	2.6	94.2	4.5	92.5	2.7	1.0	0.6
530	40	97.8	2.8	74.7	7.3	85.2	3.6	2.5	1.3
550	40	96.0	8.6	76.0	21.7	70.0	5.0	4.5	1.4
550	20	85.7	10.0	57.1	12.7	78.6	4.5	11.0	3.0
550 •	42	90.4	10.7	78.1	45.8	29.5	2.0	3.7	0.2
580	41	65.9	11.8	50.9	30.4	62.5	5.5	9.1	1.8
600	42	63.1	15.5	40.2	34.5	53.6	8.3	18.4	4.8
630	42	62.0	9.9	38.2	22.1	58.8	12.3	15.9	8.0

•The experiment was run in the absence of hydrogen. The other experiments were run in a hydrogen atmosphere (passage rate 2 liters per hour).

EXPERIMENTAL

Tetraethylsilane was obtained in 83% yield by reacting C_2H_5MgBr with $SiCl_4$ [3]; after distillation from metallic sodium it had the following constants:

B.p. 150.5-152.1° (756.5 mm), d_4^{20} 0.7660, n_D^{20} 1.4268.
Literature [1]: B.p. 152.2° (760 mm), d_4^{20} 0.7657, n_D^{20} 1.4268.

Operation technique of the catalytic experiments. The experiments were run in the usual catalytic apparatus of the flow type. The catalyst was prepared by the procedure given in [4], and represented chromium trioxide deposited on the γ-form of aluminum oxide, with small additions of potassium and cerium. The activity of the catalyst was verified by its dehydrocyclization of n-heptane (by the method of Moldavsky and Kamusher [4]). In this connection the amount of aromatic hydrocarbons in the condensate was of the order of 65-70%, which indicated that the catalyst was quite active. The activity of the catalyst was checked periodically during experimentation. After four to five experiments the catalyst usually lost its activity, possibly due to the deposition of elementary silicon on the active centers. Regeneration of the catalyst by blowing air through it at 500-520° did not restore its former activity; consequently, after four experiments a new portion of catalyst was usually charged into the apparatus. All of the experiments were run in a hydrogen stream (2 liters per hour). The obtained products were condensed in a coil condenser and collected in a receiver. The gaseous products were collected in a graduated gasometer.

Method of analysis. The condensates from the experiments were distilled through a rectification column. The obtained fractions were analyzed for their triethylsilane content by the refractive index method. On the basis of our earlier derived linear equation [1]: $\%(C_2H_5)_3SiH = 6803(1.4268 - n_D^{20})$,• and the table attached to it, we constructed a graph showing the relationship between the triethylsilane content in a binary mixture of tetraethylsilane and triethylsilane and the index of refraction. With the aid of this it proved possible to determine the triethylsilane content in the obtained condensate fractions.

The gaseous reaction products were analyzed using a gas analyzer designed by the All-Union Heat Engineering Institute. The gas was analyzed for the amount of CO_2, olefins, CO, H_2 and paraffins.

•In the text of the cited paper (page 271) there appears an obvious error: $\%(C_2H_5)_3SiH = 6803(n_D^{20} - 1.4268)$.

Identification of the reaction products. Distillation of the various condensates gave the fractions: 1) 105-120°; 2) 140-152°, and residue. After being analyzed for their $SiH(C_2H_5)_3$ and $Si(C_2H_5)_4$ content, all of the fractions from the various distillations with the same boiling point were combined and redistilled through a column, for the purpose of isolating the individual substances and their identification.

The 1st fraction was almost pure triethylsilane. After redistillation it had the constants:

B.p. 107.0-107.7° (756.5 mm), d_4^{20} 0.7315, n_D^{20} 1.4121.
Literature [1]: B.p. 108.0° (756 mm), d_4^{20} 0.7311, n_D^{20} 1.4121.
Found M: 116.3, 115.7. $C_6H_{16}Si$. Calculated M: 116.3.

The 2nd fraction was predominantly unreacted tetraethylsilane, which after redistillation had the constants:

B.p. 150.5-152° (756 mm), d_4^{20} 0.7651, n_D^{20} 1.4268.

The residues, representing not more than 3-6% of the passed tetraethylsilane, were not studied closer.

Bromination of the unsaturated hydrocarbons contained in the gas from the experiments at 600-630°. The passage of 11 liters of the gas resulted in the decolorization of 5 ml of bromine. The product after drying over $CaCl_2$ was distilled and proved to be 1,2-dibromoethane:

B.p. 130.0-131.5° (766.3 mm), d_4^{20} 2.1791, n_D^{20} 1.5375.
Literature [5]: B.p. 131.6° (760 mm), d_4^{20} 2.1785, n_D^{20} 1.53789.

Qualitative test for the silicon deposited on the catalyst. The finely pulverized catalyst was treated in a platinum crucible with hydrofluoric acid. The liberation of SiF_4 here was shown by the fact that a drop of water, contained in a platinum wire loop and held in the vapors of the evolved gas, became turbid.

The Raman spectrum of the 140-152° fraction shows lines that correspond to some of the lines from the spectrum of tetraethylsilane (389, 1416, 1461 cm^{-1}) [6], and also a weak line with a frequency of 2100 cm^{-1}. From [7] the 2118 cm^{-1} frequency in the spectrum of trimethylsilane is the frequency of the Si–H valence vibration. The spectrum taken by us does not show any lines corresponding to the characteristic frequency for the double bond in α-alkenylsilanes $>SiCH{=}CH_2$ (1591 cm^{-1}, according to [8]).

SUMMARY

Tetraethylsilane on a chromium catalyst at 530-600° in a hydrogen atmosphere suffers decomposition into triethylsilane and ethylene. Further elevation of the temperature leads to profound hydrogenolysis with the formation of ethane and silicon. Dehydrogenation of tetraethylsilane does not take place under the indicated conditions.

LITERATURE CITED

[1] M. G. Voronkov, B. N. Dolgov and G. B. Karpenko, J. Gen. Chem. 24, 269 (1954) (T.p. 271).*

[2] C. E. Waring, Trans. Faraday Soc. 36, 1142 (1940); D. F. Helm and E. Mack, J. Am. Chem. Soc. 59, 60 (1937); T. V. Sathyamurthy, S. Swamynathan and L. M. Geddanapally, J. Indian Chem. Soc. 27, 509 (1950).

[3] S. N. Ushakov and A. M. Itenberg, J. Gen. Chem. 7, 2495 (1937).

[4] V. I. Isagulyants and G. M. Egorova, Chemistry of Petroleum (1948), p. 232.

[5] Beilst. 1, 90.

[6] M. V. Volkenshtein and E. I. Pokrovsky, Bull. Acad. Sci. USSR, Div. Chem.Sci. 1953, No. 1, 177 (T.p. 159).*

[7] V. A. Kolesova, E. V. Kukharskaya and D. N. Andreev, Bull. Acad.Sci. USSR, Div. Chem. Sci. 1953, No. 2, 294 (T.p. 267).*

[8] A. D. Petrov and V. F. Mironov, Progr. Chem. 22, 404 (1953).

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*T.p. = C. B. Translation pagination.

Identification of the reaction products. Distillation of the [illegible] gave the fractions: 1) 126-130°, 2) 145-165°, and residue. [illegible] of the fractions [illegible] through a column for the purpose of [illegible]

The 1st fraction, [illegible]

B.p. 127.5-128.5° [illegible]
Literature [illegible]
Found M: [illegible]

The 2nd fraction [illegible]

B.p. 150.5-152° [illegible]

The residue [illegible]

Examination of the structure of [illegible] The passage of 11 liters of the gas [illegible] over $CaCl_2$, was distilled and [illegible]

B.p. 130.5-131.5° [illegible]
Literature [6]: B.p. [illegible]

Confirmation was [illegible] a platinum crucible with hydrofluoric acid. The [illegible] water, contained in a platinum [illegible]

The Raman spectrum of the 140-152° fraction [illegible] (985, 1414, 1640 cm^{-1}) [illegible] from [7] the 2118 cm^{-1} frequency in the spectrum of [illegible]

SUMMARY

[illegible]

LITERATURE CITED

[1] M. G. Voronkov, B. N. Dolgov and [illegible]

[2] [illegible] Trans. Faraday Soc. 30, [illegible]

[3] [illegible]

[4] V. I. [illegible] and G. M. [illegible] Chemistry of [illegible]

[5] M. V. [illegible]

[7] V. A. [illegible]

[8] A. D. Petrov and V. F. Mironov, [illegible]

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HETEROFUNCTIONAL CONDENSATION OF ORGANOETHOXY- AND ORGANOCHLOROSILANES

K.A. Andrianov, T.N. Ganina and N.N. Sokolov

Earlier we had communicated on the heterofunctional condensation of organoalkoxy- and organochlorosilanes with organoacetoxysilanes, leading to the formation of polyorganosiloxanes [1]. In expanding these studies we investigated the heterofunctional condensation of organoethoxysilanes with organochlorosilanes. Here experiment revealed that very slight reaction occurred when methylphenyldichlorosilane was heated with phenyltriethoxysilane, dimethyldichlorosilane with phenyltriethoxysilane, and ethylphenyldiethoxysilane with phenyltrichlorosilane in the absence of catalysts. However, in the presence of catalysts such as ferric chloride and aluminum chloride, the heterofunctional condensation proceeds with the formation of polyorganosiloxanes.

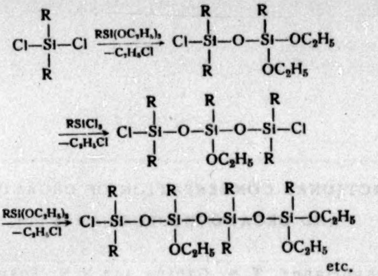
When methylphenyldichlorosilane is reacted with phenyltriethoxysilane in the presence of either ferric chloride or aluminum chloride, the amount of chlorine and ethoxyl groups in the condensation product drops rapidly, and there is a corresponding increase in the amount of evolved ethyl chloride. Thus, for example, the heating at 95-100° of equimolar amounts of methylphenyldichlorosilane and phenyltriethoxysilane in the presence of 1% ferric chloride for 30 minutes leads to a reduction of the chlorine content in the reaction mixture from 17.40 to 1.47%, to a reduction of the ethoxyl groups from 23.97 to 1.0%, and to the evolution here of ethyl chloride in 65.44% of the theoretical amount.

The reaction proceeds at a slower rate in the presence of aluminum chloride. The amount of catalyst also exerts essential influence on the kinetics of the reaction. When the amount of aluminum chloride is increased from 0.25 to 1.0% the time required to achieve approximately the same degree of reaction drops from 56 to 6.5 hours. Ferric chloride proved to be a more active catalyst than aluminum chloride: if with aluminum chloride the reaction requires hours, then with ferric chloride it is essentially complete in 25-45 minutes.

In Fig. 1 is shown the reaction kinetics for the condensation of 0.9 mole of methylphenyldichlorosilane with 0.6 mole of phenyltriethoxysilane in the presence of 1.0% aluminum chloride (in the figure the amounts of Cl and OC_2H_5 are given in percents of their initial amounts, which is taken as 100%). In Fig. 2 is shown the comparative rate of decrease in the chlorine content when ferric chloride is used (0.9 mole of methylphenyldichlorosilane and 0.6 mole of phenyltriethoxysilane with 0.25% ferric chloride) and when aluminum chloride is used (1.37 moles of methylphenyldichlorosilane and 1 mole of phenyltriethoxysilane with 0.25, 0.6 and 1.0% aluminum chloride).

The condensation also proceeds with dimethyldichlorosilane and phenyltriethoxysilane. Here the same rules as before are observed relative to the influence of catalysts, their amount, and also the influence of temperature on the reaction course. In Fig. 3 is shown the kinetics for the reaction of 0.6 mole of phenyltriethoxysilane with 0.9 mole of dimethyldichlorosilane in the presence of 0.25% ferric chloride. The reaction kinetics for the condensation of 0.6 mole of ethylphenyldiethoxysilane with 0.4 mole of phenyltrichlorosilane in the presence of 1% aluminum chloride is shown in Fig. 4 (the amounts of Cl and OC_2H_5 are given in percents of the initial amounts).

An examination of the experimental data reveals that the heterofunctional condensation of alkyl (aryl) halosilanes with alkyl(aryl) ethoxysilanes leads to the formation of polymeric products – the polyorganosiloxanes. The formation of the polyorganosiloxanes proceeds by the scheme of stepwise condensation and is accompanied by the evolution of ethyl chloride and an increase in the viscosity of the polymer. In general the reaction for the formation of polyorganosiloxanes can be depicted as follows:



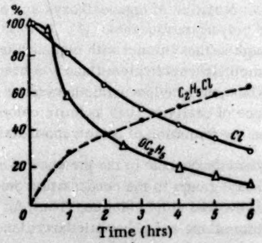


Fig. 1. Reaction of methylphenyldichlorosilane with phenyltriethoxysilane (catalyst – 1% aluminum chloride). Explanation in text.

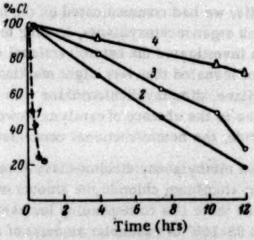


Fig. 2. Reaction of methylphenyldichlorosilane with phenyltriethoxysilane. 1) 0.25% ferric chloride, 2) 1.0% aluminum chloride, 3) 0.6% aluminum chloride, 4) 0.25% aluminum chloride.

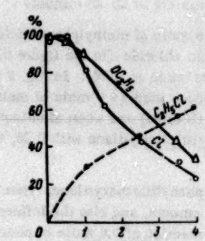


Fig. 3. Reaction of phenyltriethoxysilane with dimethyldichlorosilane (catalyst – 0.25% ferric chloride).

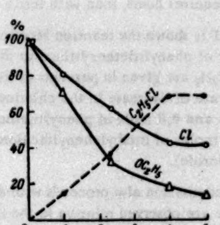


Fig. 4. Reaction of ethylphenyldiethoxysilane with phenyltrichlorosilane (catalyst – 1% aluminum chloride).

Due to the presence of a trifunctional component the ethoxy groups of the polymeric molecule react with alkyl (aryl) halosilanes to yield not only linear, but also branched-chain molecules. If the condensation is carried too far, polymers with condensed chains in the molecule are formed as insoluble gelatinous substances.

EXPERIMENTAL

Starting substances: dimethyldichlorosilane, chlorine content 55.20% (calc. 54.98); methylphenyldichlorosilane, 34.18% (37.17); phenyltrichlorosilane, 50.1% (50.31); phenyltriethoxysilane, ethoxy group content 54.36% (calc. 56.25); phenylethyldiethoxysilane, 40.80% (40.17).

The calculations were based on 100% products. In all cases the condensation was run in a three-necked flask with an airtight seal for the stirrer, thermometer, dropping funnel and reflux condenser; the condenser was connected to a trap placed on liquid nitrogen to trap the ethyl chloride.

Each condensation was run with stirring at a given temperature. Samples were taken during reaction and analyzed for their content of chlorine and ethoxyl groups. The ethyl chloride was identified by its boiling point (12.5-13°). The condensation products are light brown viscous liquids.

The amounts of reagents taken, the reaction conditions and the condensation results of methylphenyldichlorosilane with phenyltriethoxysilane are given in Table 1. For two of the experiments (nos. 7 and 8) chlorine and silicon balances were made, showing satisfactory agreement of the calculated and obtained data (Table 2).

TABLE 1

Expt. No.	Reagents: methylphenyldichlorosilane (in g)	Reagents: phenyltriethoxysilane (in g)	Amount in starting mixture (in %): Cl	Amount in starting mixture (in %): OC_2H_5	Catalyst (in %): aluminum chloride	Catalyst (in %): ferric chloride	Reaction conditions: temperature	Reaction conditions: time (hours)	Yield of condensation product (in g)	Amount in condensation product (%): Cl	Amount in condensation product (%): OC_2H_5	Amount of ethyl chloride (in % of the theoretical)
1	171.9	144	17.51	23.97	—	0.25	95—100°	0.75	267	3.93	4.0	64.20
2	171.9	144	17.51	23.97	—	0.50	95—100	0.42	263	2.11	6.16	56.20
3	171.9	144	17.52	23.98	—	1.00	95—100	0.5	240	1.47	1.0	65.44
4	146.1	134	17.30	23.55	0.25	—	145—150	56	213	6.16	5.0	—
5	146.1	134	17.30	23.45	0.60	—	130—140	12.5	209.5	3.57	3.0	—
6	146.1	134	17.35	23.50	1.0	—	130—140	14.5	207	2.30	2.8	—
7	171.9	144	17.51	24.0	1.0	—	130—132	6.5	264	5.10	1.8	63.70
8	171.9	144	17.51	24.0	1.0	—	130—132	5.0	239	7.95	2.8	68.4

TABLE 2

Expt. No.	Before reaction (in g): chlorine	Before reaction (in g): silicon	After reaction (in g): found	After reaction (in g): chlorine	After reaction (in g): silicon
8	82.44	54.61	In the condensation product	25.20	53.70
			In the ethyl chloride	58.25	—
			Total	83.45	53.70
7	60.16	—	In the condensation product	13.46	—
			In the ethyl chloride	46.20	—
			Total	59.66	—

TABLE 3

Expt. No.	Reagents (in g)		Amount in starting mixture (in %)		Catalyst (in %)		Reaction conditions		Yield of condensation product (in g)	Amount in condensation product (%)		Amount of ethyl chloride (in % of the theoretical)
	dimethyldichlorosilane	phenyltriethoxysilane	Cl	OC_2H_5	aluminum chloride	ferric chloride	temperature	time (hours)		Cl	OC_2H_5	
9	116.1	144	24.0	32.0	—	0.25	65—66°	4	170.65	5.21	10.65	59.86
10	116.1	144	24.0	32.0	—	0.25	66—67	2	200.0	5.60	11.0	50.0
11	116.1	144	25.2	32.1	1.0	—	66—67	5.5	266.5	24.30	30.9	—
12	129	240	18.8	34.0	1.0	—	60 100 120	15 + 5 + 3	180.0	5.14	1.92	—

The condensation of dimethyldichlorosilane with phenyltriethoxysilane is shown in Table 3.

For the condensation of ethylphenyldiethoxysilane with phenyltrichlorosilane we took: 0.6 mole of ethylphenyldiethoxysilane, 0.4 mole of phenyltrichlorosilane and 1% (2.19 g) of aluminum chloride. The reaction was run at 145-150° for 5 hours. The weight of product after reaction was 152 g, and the weight of ethyl chloride was 52 g (67.10%).

SUMMARY

1. The thermal condensations of dimethyldichlorosilane, methylphenyldichlorosilane and phenyltrichlorosilane with phenyltriethoxysilane and ethylphenyldiethoxysilane were studied in the presence of catalysts.

2. It was established that polyorganosiloxanes are formed in the condensations with the liberation of ethyl chloride during the reaction process.

3. It was found that a good catalyst for the reaction is ferric chloride.

LITERATURE CITED

[1] K. A. Andrianov, N. N. Sokolov and E. N. Khrustaleva, J. Gen. Chem. 26, 1102 (1956) (T.p. 1249).*

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*T.p. = C. B. Translation pagination.

OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

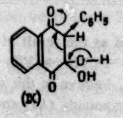
XXV. THE HYDROLYTIC AND OXIDATIVE-HYDROLYTIC CLEAVAGE OF 2-PHENYL- AND 2-BENZYL-3-HYDROXY-1,4-NAPHTHOQUINONES•

L.A. Shchukina and E.P. Semkin

In earlier communications we had shown [2,3] that when boiled in aqueous buffer solutions, having a pH above 7, 3-hydroxy-1,4-naphthoquinone (I; R = H) and 2-methyl-3-hydroxy-1,4-naphthoquinone (I; R = CH_3) are capable of hydrolytic cleavage with the formation of compounds of the type (III $\rightleftharpoons$ IV), which at times could even suffer further transformations. Later, on the example of 6-methyl-3-hydroxy-1,4-benzoquinone we were able to show experimentally [4] that the cleavage of hydroxyquinones proceeds in two stages: at first their hydration products of the II type are formed, and it is only after this that the latter undergo hydrolytic cleavage, in which connection the first stage is easily realized in neutral medium, while the second stage is usually possible only when the solution pH exceeds 7.••

To understand more fully the essence and character of the hydrolytic cleavage shown by hydroxyquinones, it seemed of interest to make a study of the degree of influence shown on this process by the nature of the substituents found in the 2 position of the quinone ring; consequently, we decided to extend our earlier studies to the hydroxynaphthoquinones containing either an aryl or aralkyl radical in the 2 position, and specifically to the 2-phenyl- and 2-benzyl-3-hydroxy-1,4-naphthoquinones (I; R = C_6H_5 and $CH_2C_6H_5$). In this communication we give the results of studying the hydrolytic and oxidative-hydrolytic transformations of these two quinones in comparison with the data described in previous studies [2,3].

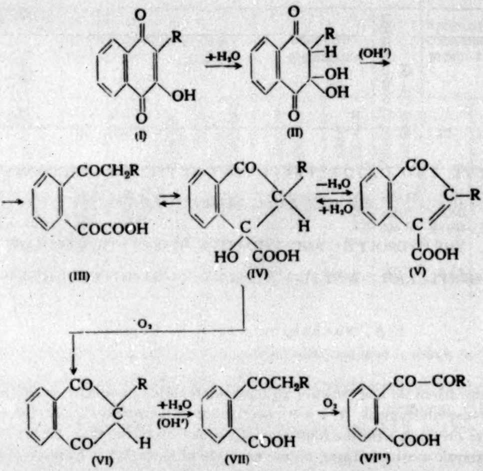
When boiled in aqueous buffer solutions, both in the presence and absence of atmospheric oxygen, all four of the investigated hydroxyquinones (I; R = H, CH_3, $CH_2C_6H_5$ and C_6H_5) behave the same at first, suffering only hydrolytic cleavage. In accord with our expectations the most easily changed of these quinones proved to be the 2-phenyl-3-hydroxy-1,4-naphthoquinone, since its phenyl group, functioning as a fairly strong electron acceptor, facilitates both the hydration and hydrolytic cleavage of the molecule (see Formula IX). In contrast to the other three quinones, this quinone is capable of showing slow cleavage even when boiled with water, and at a pH of about 7.5 its cleavage proceeds at a fairly rapid rate. On the other hand, as was to be expected, 2-benzyl-3-hydroxy-1,4-naphthoquinone is cleaved with considerably greater difficulty. In this case the process begins only at a pH of about 7.5, i.e. under



(IX)

•See [1] for Communication XXIV on the oxidative and oxidative-hydrolytic transformations of organic molecules.

••These data tend to refute the hypothesis recently expressed by Fieser relative to the mechanism of the hydrolytic cleavage of hydroxyquinones [5], in accord with which only the anion of the hydroxyquinone can show hydration, requiring the presence of an alkaline medium, since subsequent hydrolytic cleavage processes (or rearrangement of the benzilic acid type) are realized in the absence of alkali. Fieser's theory relative to the benzilic acid type of rearrangement also stands in contradiction to the ability of the primary cleavage products of hydroxyquinones to undergo tautomeric transformations of the type (III $\rightleftharpoons$ IV), a situation observed by us many times in recent years [2-4,6].



approximately the same conditions as for 2-methyl-3-hydroxy-1,4-naphthoquinone [2]. When the reaction is run in a nitrogen atmosphere it is always possible to isolate in various amounts the original hydrolytic cleavage product of the starting quinone – corresponding to the acid (III $\rightleftharpoons$ IV), together with which its dehydration product – the indonecarboxylic acid (V)* – is usually formed. The latter was also obtained in greater yield (95%) from 2-phenyl-3-hydroxy-1,4-naphthoquinone, evidently due to the fact that here the phenyl radical greatly increases the mobility of the hydrogen atom found on the same carbon atom.

It is interesting to mention that in the hydrolytic cleavage of hydroxyquinones in boiling buffer solutions an equilibrium is apparently always established between the compound (III $\rightleftharpoons$ IV) formed from a given quinone and its dehydration product (V). Thus, for the 2-phenyl- and 2-benzyl-3-hydroxy-1,4-naphthoquinones we were able to show experimentally not only mutual interchange of the corresponding compounds (III $\rightleftharpoons$ IV) and V when their solutions, having a pH of about 7.5, were boiled, but also the presence of equilibrium between these compounds.** Although the presence of atmospheric oxygen is practically without effect on the hydrolytic cleavage stage of the studied hydroxyquinones, still for 2-phenyl-3-hydroxy-1,4-naphthoquinone the originally formed acid (III $\rightleftharpoons$ IV) proved to be capable of showing further easy changes, being transformed into 2-phenyl-1,3-indandione (VI) and o-carboxybenzil (VIII).

It was postulated, and experimentally confirmed later, that these compounds are formed as the result of the following series of alternate oxidative and hydrolytic transformations: (I)→(II)→(III)$\rightleftharpoons$(IV)→(VI)→(VII)→(VIII) (see scheme; R = C_6H_5). Actually, it was shown that compound (III$\rightleftharpoons$IV), and also acid (V), behave in the same manner as 2-phenyl-3-hydroxy-1,4-naphthoquinone (I), under similar conditions forming compounds (VI) and (VIII). In turn, the 2-phenyl-1,3-indandione (VI) is transformed under the same conditions, but in the absence of atmospheric oxygen, into desoxybenzoin-o-carboxylic acid (VII), and in its presence – into the final o-carboxybenzil (VIII). And finally, compound (VII) also proved capable of being quantitatively oxidized by atmospheric oxygen in boiling buffer solution at a pH of about 7.5 into o-carboxybenzil (VIII).*** As a result, the whole path of the oxidative-hydrolytic transformations of 2-phenyl-3-hydroxy-1,4-naphthoquinone can be considered as having been completely elucidated.

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*An exception is the hydrolytic cleavage of 3-hydroxy-1,4-naphthoquinone, yielding only the o-acetylphenylglyoxylic acid (III$\rightleftharpoons$IV; R = H).

**See Tables 1 and 2 in the experimental section.

***See Table 1 in the experimental section.

In conclusion we should briefly discuss the question of the structure shown by our again obtained compounds ($III \rightleftharpoons IV$) and (V) with R = C_6H_5 and $CH_2C_6H_5$. Since they all belong to already known types of compounds, it seemed superfluous to us to make a special study of them, with the exception however of the 2-phenylindone-3-carboxylic acid (V; R = C_6H_5), since in its properties this compound proved to be sharply different from the compound already described in the literature under the same name [7]. Our acid is a bright red crystalline substance with m.p. 197-198°. The carbonyl and carboxyl groups present in its molecule were characterized by preparing the semicarbazone, and also by preparing the methyl and ethyl esters, in which connection the molecular weight of the ethyl ester was determined. The presence of a double bond was established by preparing the monoxide (for more details see Communication XXVII [8]), and also the hydration product, which proved to be identical with compound ($III \rightleftharpoons IV$; R = C_6H_5). And finally, the presence of the carbon skeleton of indan in the molecule was shown by oxidation of the substance with H_2O_2 in alkaline medium to the 2-phenyl-1,3-indandione (VI). All of these data leave no doubt that the acid with m.p. 197-198° is actually 2-phenylindone-3-carboxylic acid.

As regards the compound described in the literature under the same name [7], it was obtained as the result of exposing diphenylmaleic and diphenylfumaric acids to ultraviolet illumination [9]. This compound is a white substance with m.p. 315°, characterized only as the methyl ester with m.p. 91°. No other data that would permit judging its structure are found in the literature, and the formula of 2-phenylindone-3-carboxylic acid assigned to it was purely arbitrary. It is evident that this postulation should now be considered erroneous.

EXPERIMENTAL

1. Hydrolytic and oxidative-hydrolytic cleavage of 2-phenyl-3-hydroxy-1,4-naphthoquinone (I; R = C_6H_5).

a) In a nitrogen atmosphere. Using the earlier described apparatus (Communication XXII, Expt. 1 [14]) a mixture of 12 g of 2-phenyl-3-hydroxy-1,4-naphthoquinone* and 3 liters of phosphate buffer solution (pH 7.4; capacity 0.15 mole) was boiled for 15 hours in a nitrogen atmosphere. Then the solution was evaporated in a nitrogen atmosphere to a volume of 300 ml, 70 ml of 30% H_2SO_4 was added, and after 30-40 minutes the red precipitate of 2-phenylindone-3-carboxylic acid (V; R = C_6H_5) was filtered. Weight 11.5 g (95%); m.p. 196-197° (from glacial CH_3COOH). The water solution was extracted 5 times with ether, the ether solution was dried over Na_2SO_4, and the ether was distilled. The residue was 0.9 g of slowly crystallizing oily substance. Two recrystallizations from CH_3COOH gave 0.5 g (4%) of o-phenacetylphenylglyoxylic acid ($III \rightleftharpoons IV$; R = C_6H_5) with m.p. 161-162°.

The hydrolytic cleavage and other transformations of compounds ($III \rightleftharpoons IV$), (V) and (VI) with R = C_6H_5 were studied under completely analogous conditions. Each of these substances was taken in an amount of 1 g, while the resulting compounds were isolated the same as described above. Only for the hydrolytic cleavage of compound (VI) was the obtained desoxybenzoin-o-carboxylic acid (VII) extracted with ether directly after the reaction solution had been made acid; its m.p. 74° [15] (from 20% CH_3COOH). The obtained results are summarized in Table 1. In addition, we ran the hydrolytic cleavage of 2-phenyl-3-hydroxy-1,4-naphthoquinone with observance of all of the conditions described above, but in water solution for 30 hours. On conclusion of reaction we isolated 75% of unchanged starting quinone and 17% of 2-phenyl-indone-3-carboxylic acid.

b) In an atmosphere of air. A solution of 3 g of 2-phenyl-3-hydroxy-1,4-naphthoquinone in 1 liter of phosphate buffer solution (pH 9.2; capacity 0.15 mole) was boiled for 48 hours, constantly passing a stream of CO_2-free air through the solution. Then 30 ml of 30% H_2SO_4 was added and the resulting precipitate was recrystallized from 50% alcohol. We obtained 1 g (38%) of 2-phenyl-1,3-indandione (VI; R = C_6H_5) with m.p. 145-146° [16], while the alcohol solution (after dilution with water) yielded 0.3 g (10%) of 2-phenylindone-3-carboxylic acid with m.p. 197° (from glacial CH_3COOH). The acid aqueous mother liquor obtained above was extracted 5 times with ether. After the ether was distilled off, the residue was recrystallized from 50% CH_3COOH. Here we obtained 0.15 g (16%) of o-carboxybenzil (VIII; R = C_6H_5) with m.p. 140-141° [17].

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*This quinone can be obtained by treating 2-hydroxyl-1,4-naphthoquinone with benzoyl peroxide in acetic acid solution at 115°, but here the yield fails to exceed 15% (see [10]). A more expedient synthesis is to start with ethyl phenylacetate, going through the α,γ-diphenylacetoacetic ester and 2-phenyl-1,3-dihydroxynaphthalene, the oxidation of the latter leading directly to 2-phenyl-3-hydroxy-1,4-naphthoquinone [11-13]. The melting point of this quinone is 147° (from methanol); yield 35%, based on ethyl phenylacetate.

The oxidative-hydrolytic cleavage of compounds (III$\rightleftharpoons$IV), (V), (VI) and (VII) with R = C_6H_5 was realized under analogous conditions. Each of these compounds was taken in an amount of 1 g. The obtained data are summarized in Table 1.

TABLE 1

Starting compound (R = C_6H_5)	Hydrolytic transformations under the conditions of Expt. 1a			Oxidative-hydrolytic transformations under the conditions of Expt. 1b		
	yield of compound (R = C_6H_5) (in %)					
	III$\rightleftharpoons$IV	V	VII	V	VI	VIII
I	4	95		10	38	16
III$\rightleftharpoons$IV	4	95			37	25
V	4	95			40	37
VI			100			85
VII						100

2. Properties of o-phenacetylphenylglyoxylic acid (III$\rightleftharpoons$IV; R = C_6H_5). This compound crystallizes from acetic acid as colorless needles with m.p. 162°.

Found %: C 71.89; H 4.82. M (titration) 266. $C_{15}H_{11}O_2COOH$. Calculated %: C 71.64; H 4.48. M 268.

When boiled with CH_3OH in the presence of H_2SO_4, o-phenacetylphenylglyoxylic acid is transformed into the methyl ester of 2-phenylindone-3-carboxylic acid (see Expt. 3), and when heated for 15 minutes with concentrated H_2SO_4 at 100° it is quantitatively transformed into 2-phenylindone-3-carboxylic acid, which is isolated by pouring the reaction mass over ice. For the other transformations of o-phenacetylphenylglyoxylic acid see Expts. 1a and 1b.

3. Properties of 2-phenylindone-3-carboxylic acid (V; R = C_6H_5). This compound crystallizes from glacial acetic acid as bright red tetrahedral pyramids with m.p. 197-198°.

Found %: C 76.65; H 3.88. $C_{16}H_{10}O_3$. Calculated %: C 76.80; H 4.00. Number of active hydrogen atoms 1.02 (determined by the method of Terentyev).

The methyl ester was obtained by heating the acid (V; R = C_6H_5) with CH_3OH in the presence of H_2SO_4 for 8 hours. M.p. 121° (from diisoamyl ether).

Found %: C 77.15; H 4.70. $C_{17}H_{12}O_3$. Calculated %: C 77.27; H 4.55.

The ethyl ester was obtained in the same manner as the methyl ester. M.p. 51° (from diisoamyl ether).

Found %: C 77.66; H 5.13. M (in nitrobenzene) 280. $C_{18}H_{14}O_3$. Calculated %: C 77.69; H 5.03. M 278.

The semicarbazone was obtained by heating an alcohol solution of the acid (V; R = C_6H_5) with semicarbazide hydrochloride and potassium acetate for 15 minutes. Decomposition point 234-235° (from 50% alcohol).

Found %: C 66.28; H 4.03; N 13.84. $C_{17}H_{13}O_3N_3$. Calculated %: C 66.45; H 4.23; N 13.68.

Oxidation of the acid (V; R = C_6H_5) with hydrogen peroxide in the presence of 1.5% NaOH solution at 95° gave 2-phenyl-1,3-indandione in 75% yield; m.p. 146° (from 50% acetone).

TABLE 2

Starting compound ($R = CH_2C_6H_5$)	Yield of compound: ($R = CH_2C_6H_5$)	
	$III \rightleftarrows IV$	V
I	16	66
$III \rightleftarrows IV$	15	65
V	15	65

For the other transformations of 2-phenylindone-3-carboxylic acid see Expts. 1a and 1b above, and also Communication XXVII, Expt. 2c [8].

4. Hydrolytic cleavage of 2-benzyl-3-hydroxy-1,4-naphthoquinone ($I; R = CH_2C_6H_5$). A solution of 3 g of the quinone [18] in 1 liter of phosphate buffer solution (pH 7.4; capacity 0.15 mole) was boiled for 72 hours in a nitrogen atmosphere under the conditions of Expt. 1a. On conclusion of reaction, the solution was evaporated in a nitrogen atmosphere to a volume of 300 ml, cooled, filtered from a small amount of tarry substance, and then 25 ml of 30% H_2SO_4 was added. The resulting yellow precipitate of 2-benzylindone-3-carboxylic acid ($V; R = CH_2C_6H_5$) was filtered. Weight 1.8 g; m.p. 204° (from CH_3OH).

Found %: C 77.46; H 4.53. $C_{17}H_{12}O_3$. Calculated %: C 77.27; H 4.53.

The aqueous mother liquor was extracted 5 times with ether, the ether solution was dried over Na_2SO_4, and the ether was removed by distillation. The residue (0.9 g) was recrystallized from 10 ml of CH_3OH, as a result of which another 0.2 g of the acid ($V; R = CH_2C_6H_5$) with m.p. 204° was obtained. The total yield of this acid was 66%. The alcohol mother liquor was gradually diluted with 50 ml of water, which gave a white precipitate of o-(β-phenylpropionyl)-phenylglyoxylic acid ($III \rightleftarrows IV; R = CH_2C_6H_5$). Weight 0.5 g (16%); m.p. 179° (from 50% CH_3OH).

Found %: C 72.01; H 4.87. $C_{17}H_{14}O_4$. Calculated %: C 71.83; H 4.93.

The mutual transformation of compounds ($III \rightleftarrows IV$) and (V) with $R = CH_2C_6H_5$ was accomplished under conditions similar to those described above for the quinone ($I; R = CH_2C_6H_5$). In both cases the starting compounds were taken in amounts of 1 g. The obtained results are summarized in Table 2.

SUMMARY

1. The hydrolytic and oxidative-hydrolytic transformations of 2-phenyl- and 2-benzyl-3-hydroxy-1,4-naphthoquinones were studied and it was shown that the phenyl radical greatly facilitates hydrolytic cleavage of the quinone ring.

2. On the examples of 2-phenyl- and 2-benzyl-3-hydroxy-1,4-naphthoquinones, it was established that the compound of type ($III \rightleftarrows IV$), formed during the cleavage process of quinones, is found in the reaction solution in equilibrium with the corresponding dehydration products of the type of (V).

3. It was shown that in the presence of atmospheric oxygen the 2-phenyl-3-hydroxy-1,4-naphthoquinone is capable of very extensive oxidative-hydrolytic transformations, leading finally to the formation of o-carboxybenzil.

LITERATURE CITED

[1] M. M. Shemyakin and L. A. Shchukina, Problems of Chemical Kinetics, Catalysis and Reactivity (Acad. Sci. USSR Press, 1955), 75.

[2] L. A. Shchukina, A. P. Kondratyeva and M. M. Shemyakin, J. Gen. Chem. 18, 2122 (1948).

[3] L. A. Shchukina, A. S. Khokhlov and M. M. Shemyakin, J. Gen. Chem. 21, 908 (1951) (T.p. 997).•

[4] L. A. Shchukina, J. Gen. Chem. 22, 668 (1952) (T.p. 733).•

[5] L. F. Fieser and A. Bander, J. Am. Chem. Soc. 73, 681 (1951).

[6] L. A. Shchukina, Yu. B. Shvetsov and M. M. Shemyakin, J. Gen. Chem. 21, 346 (1951) (T.p. 381)•; D.P. Vitkovsky and M. M. Shemyakin, J. Gen. Chem. 21, 547 (1951) (T.p. 607).•

•T.p. = C. B. Translation pagination.

[7] Mme. Ramart-Lucas and J. Hoch, Ann. chim. (10), 13, 385 (1930).

[8] L. A. Shchukina and M. M. Shemyakin, J. Gen. Chem. 26, 1708 (1956) (T.p.).•

[9] A. Delisle, Ann. 269, 92 (1892).

[10] L. F. Fieser, E. Berliner and others, J. Am. Chem. Soc. 70, 3203 (1948).

[11] J. Volhard, Ann. 296, 1 (1897).

[12] G. Soliman and R. West, J. Chem. Soc. 1944, 53.

[13] G. Soliman and A. Latif, J. Chem. Soc. 1944, 55.

[14] O. M. Shemyakina, B. M. Bogoslovsky and M. M. Shemyakin, J. Gen. Chem. 22, 675 (1952) (T.p. 739).•

[15] S. Gabriel and A. Michael, Ber. 11, 1018 (1878).

[16] S. Gabriel, Ber. 18, 3470 (1885); F. Nathanson, Ber. 26, 2576 (1893).

[17] A. Hantzsch and A. Schwiete, Ber. 49, 213 (1916); K. Schaum, Ann. 462, 204 (1928).

[18] L. F. Fieser, J. Am. Chem. Soc. 48, 2930, 3201 (1926); L. F. Fieser, J. Hartwell and A. Seligmann, J. Am. Chem. Soc. 58, 1223 (1936).

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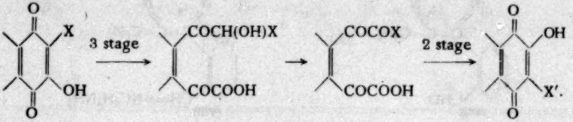
OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

XXVI. PREPARATION OF TRIKETOCARBOXYLIC ACIDS UNDER THE CONDITIONS OF THE HOOKER REACTION

L. A. Shchukina

As is known, the transformation of hydroxyquinones of type [I; $X = (CH_2)_n R$] into hydroxyquinones of type [IV; $X' = (CH_2)_{n-1} R$] under the influence of alkaline $KMnO_4$ solution is known as the Hooker reaction [1]. The mechanism of this peculiar reaction has been repeatedly subjected to independent study, and at the present time has received fairly clear elucidation [2-6]. As had been shown by us [4-6], and also by L. and M. Fieser [3], the Hooker reaction proceeds through a series of intermediate stages, in particular, through the stage of forming hydroxydiketocarboxylic acids (II) and triketocarboxylic acids (III) (for more details see [6]).



(I) (II) (III) (IV)

However, of the latter type of compounds only a single member (III; $X = CH_3$) has been isolated up to now, proving to be an extremely unstable oily substance, which could not be isolated in completely pure form or studied in sufficient detail [5]. At the same time compounds of the (III) type deserved much attention from the viewpoint of further characterization not only of the Hooker reaction, but also of the oxidative-hydrolytic transformations of organic molecules in general. Consequently, we considered it necessary to undertake a more detailed study of the formation conditions and properties of compounds of this type.

The difficulty in obtaining triketocarboxylic acids of the (III) type under the conditions of the Hooker reaction is associated with the fact that in them the radical X, usually either CH_3 or $(CH_2)_n R$, is characterized by very labile hydrogen atoms due to the strong influence exerted by the adjacent carbonyl groups. For this reason the formed acid (III) shows a tendency for rapid intramolecular condensation and subsequent transformation to the final quinones (IV). If with $X = CH_3$ the process can still be partially retarded at the stage of forming the corresponding triketocarboxylic acid (III) [5], then in the case of $X = CH_2C_6H_5$ retardation would be impossible due to the greater mobility of the hydrogen atoms in the methylene group of the benzyl radical. In this case we were able to isolate only a small amount of compound (II; $X = CH_2C_6H_5$), being the precursor of the triketocarboxylic acid.*

To avoid the described difficulties, it was decided to take the 2-aryl-3-hydroxy-1,4-naphthoquinones (I; $X = C_6H_5$, $C_6H_4CH_3$-o, β-$C_{10}H_7$), as the starting compounds, since here the triketocarboxylic acids (III) formed from them cannot undergo transformation into the quinones (IV) due to the absence of a methylene group with labile hydrogen atoms in the radical X. Actually, in all of these cases we were able to isolate the desired acids under the usual conditions of the Hooker reaction in yields ranging from 25 to 60%, which again demonstrates the validity of our opinions relative to the mechanism of this reaction [4-6]. All of the obtained acids proved to be extremely unstable colorless crystalline substances, the isolation of which required taking certain precautionary measures.

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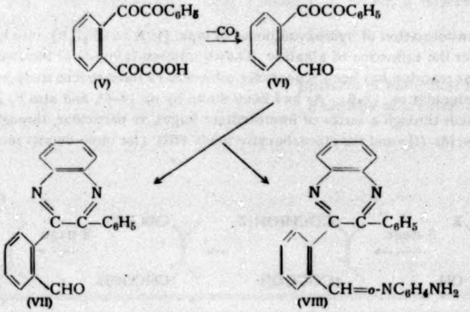
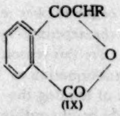
*See experimental section of this paper, Expt. 9.

Of the synthesized triketocarboxylic acids, the one studied in greatest detail by us was the acid (III; X = = C_6H_5), obtained from 2-phenyl-3-hydroxy-1,4-naphthoquinone (I; X = C_6H_5). Its structure was easily shown by its oxidative cleavage with HIO_4 to benzoic and phthalonic acids, obtained in nearly quantitative yield. The most characteristic property of this compound, which can be assigned the name of o-oxalobenzil (V), is the exceeding ease with which it cleaves a CO_2 molecule and undergoes transformation into o-formylbenzil (VI). The latter is also a very unstable substance, capable of easily suffering further changes. Nevertheless, in some cases it can be isolated in the form of its derivatives. Thus, the reaction of o-phenylenediamine with o-oxalobenzil (V) in alcohol solution results in the rapid cleavage of CO_2 and the formation of two compounds – (VII) and (VIII), obtained as a result of the formed o-formylbenzil (VI) reacting with either one or two o-phenylenediamine molecules.

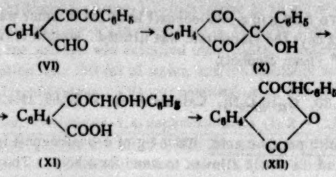


It is not only o-phenylenediamine that will effect the decarboxylation of o-oxalobenzil (V). The decarboxylation also takes place when the o-oxalobenzil is heated for a short time with various solvents, in which connection the final product usually formed here is the already known [7] benzoin-o-carboxylic acid lactone (IX; R = C_6H_5). When the o-oxalobenzil is heated with water, either in the presence or absence of atmospheric oxygen, this process is ended in 5-10 minutes, and here the lactone (IX; R = C_6H_5) is obtained in nearly quantitative yield. The other two triketocarboxylic acids (III; X = o-$C_6H_4CH_3$ and β-$C_{10}H_7$) synthesized by us behave in a similar manner, under the same conditions being converted into the corresponding lactones (IX) in high yields. It is characteristic that all of the (III) type of acids with X = Ar are capable of being decarboxylated only in acid, and not in alkaline medium, whereas acid (III) with X = CH_3 can suffer oxidative decarboxylation in alkaline medium even in the presence of atmospheric oxygen (see table). We had already discussed the mechanism of the latter reaction in detail earlier [4-6], while the mechanism for the decarboxylation of the (III) type of triketo acids with X = Ar will be examined below on the example of o-oxalobenzil (V).



(IX)

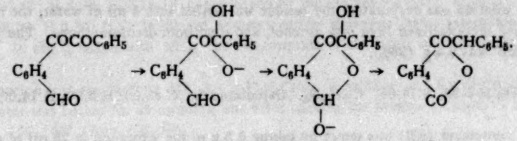
It would appear fairly obvious that the transformation of the o-oxalobenzil (V) into benzoin-o-carboxylic acid lactone (IX; R = C_6H_5) should proceed through the stage of forming o-formylbenzil (VI), the aldehyde group of which is then oxidized to a carboxyl group, while one of the ketone groups is reduced to an alcohol group. Such oxidation-reduction can be realized only as the result of intramolecular benzoin condensation and subsequent hydrolytic cleavage of the cyclic benzoin formed, or as the result of a peculiar intramolecular Cannizzaro reaction. In the first case the already known [8,9] 2-hydroxy-2-phenyl-1,3-indandione (X) should be formed as the intermediate cyclic benzoin, the hydrolytic cleavage of which can lead to benzoin-o-carboxylic acid (XI) and then to its lactone (XII).



(VI) (X) (XI) (XII)

However, we established that the boiling of 2-hydroxy-2-phenyl-1,3-indandione (X) with water does not transform it into lactone (XII) and it remains unchanged under these conditions. The formation of small amounts of lactone (XII) was observed only when the 2-hydroxy-2-phenyl-1,3-indandione was either boiled with 3% KOH solution or when it was treated with 15% KOH solution at 20°, i.e. under considerably more drastic conditions than for the transformation of o-oxalobenzil (V) into the same lactone.

Consequently, we concluded that the benzoin-o-carboxylic acid lactone is formed by the second of the paths described above, namely as the result of an intramolecular Cannizzaro reaction, proceeding between the aldehyde group and one of the ketone groups of o-formylbenzil (VI), which should lead to the direct formation of lactone (XII). It should be emphasized that similar instances of the Cannizzaro reaction are described in the literature [10]; in addition, it is well known at the present time that this reaction actually reduces to the formation of an ester. From this, in accord with contemporary theories on the mechanism of the Cannizzaro reaction [10,11], the transformation of o-formylbenzil (VI) into lactone (XII) can be depicted as follows:



(VI) (XII)

EXPERIMENTAL

1. Oxidation of 2-phenyl-3-hydroxy-1,4-naphthoquinone (I; X = C_6H_5) with potassium permanganate. To 2.7 g of the quinone [12] in 200 ml of 0.5% KOH solution at 8-10° and with vigorous stirring was added a solution, cooled to 10°, of 2.4 g of $KMnO_4$ in 200 ml of 10% KOH solution. After 15-20 minutes, after all of the $KMnO_4$ had been reduced, the MnO_2 precipitate was separated and then the solution was acidified with 230 ml of 10% H_2SO_4. The precipitate of the quinone was filtered, and the solution was extracted 5 times with ether. The ether extract was dried over Na_2SO_4 for 30 minutes, and then the ether was distilled off under slight vacuum to a volume of 4-5 ml at a bath temperature not exceeding 35-40°. The white precipitate of o-oxalobenzil was filtered and washed with a small amount of ether. Weight 1.3 g (41%); m.p. 115-116° (decomposition).

2. Properties and transformations of o-oxalobenzil (V).

a) o-Oxalobenzil is readily soluble in the usual organic solvents. It crystallizes with one mole of water from moist ether. It cannot be recrystallized in the usual manner, since it is easily decarboxylated. When the conditions of Expt. 1 are observed the o-oxalobenzil is immediately obtained in sufficiently pure form, but in case of need it is dissolved without heating, in ether (1:100), charcoal is added, the solution is filtered, and the ether is distilled off, as indicated in Expt. 1.

Found %: C 63.88; H 4.36. $C_{16}H_{10}O_5 \cdot H_2O$. Calculated %: C 64.00; H 4.00. M (determined by titration 292; calculated for $C_{15}H_9O_3COOH \cdot H_2O$ 300. When titrated with HIO_4, 0.90 mole of the latter is consumed after 4 hours.

b) o-Phenylenediamine salt. To 0.12 g of o-oxalobenzil in 50 ml of ether was added 0.15 g of o-phenylenediamine in 50 ml of ether. After 2 days the precipitate was filtered. Weight 0.12 g (77%). White slender needles with decomposition point 202° (from alcohol).

Found %: C 67.60; H 4.57; N 7.33. $C_{22}H_{18}O_5N_2$. Calculated %: C 67.69; H 4.61; N 7.18.

c) Cleavage of o-oxalobenzil with periodic acid. To 0.4 g of o-oxalobenzil in 10 ml of alcohol was added 16 ml of 0.5 N HIO_4 solution and the whole allowed to stand for 4 hours. Then 75 ml of water was added, the mixture extracted 8 times with ether, and the ether removed by distillation. The residue was treated with a solution of 0.6 g of o-phenylenediamine in 20 ml of water. After a day, 7 ml of 10% NaOH solution was added, the alkaline solution extracted 5 times with ether, then acidified with 8 ml of 10% H_2SO_4, the precipitate filtered, then boiled with 5 ml of water, and the latter added to the main solution. The weight of the phthalonic acid quinoxaline derivative was 0.35 g (98.8%); its m.p. 240° [5,6]. The aqueous solution was extracted 8 times with ether, the ether solution dried over Na_2SO_4, and the ether removed by distillation. The yield of benzoic acid was 0.15 g (92%).

d) Reaction of o-oxalobenzil with o-phenylenediamine. To 1.0 g of o-oxalobenzil in 10 ml of 60% alcohol was added 1.2 g of o-phenylenediamine in 10 ml of 60% alcohol, and after 30 minutes the bright orange precipitate was filtered. We obtained 0.4 g (37%) of compound (VII) with decomposition point 197-199° (from 80% CH_3COOH).

Found %: C 81.53; H 4.60; N 9.14. $C_{21}H_{14}ON_2$. Calculated %: C 81.29; H 4.51; N 9.03.

The alcohol mother liquor from compound (VII) was diluted with 100 ml of water and extracted 5 times with ether. The ether solution was evaporated, the residue was boiled with 5 ml of water, the hot solution filtered, and the compound recrystallized from 60% alcohol, and then from dichloroethane. The yield of compound (VIII) with m.p. 286-288° was 0.4 g (28%).

Found %: C 80.86; H 5.23; N 14.06. $C_{27}H_{20}N_4$. Calculated %: C 81.00; H 5.00; N 14.00.

The structure of compound (VII) was shown by taking 0.3 g of the substance in 75 ml of alcohol and oxidizing it with ammoniacal silver, obtained from 0.3 g of $AgNO_3$ and 10 ml of 10% NH_3. After 10 minutes charcoal was added, the solution filtered, and then extracted 5 times with ether. The ether solution was washed with 10% soda solution, the water layer made acid with H_2SO_4, and then extracted with ether. The ether solution was dried over Na_2SO_4, and the ether was removed by distillation. Here we isolated 0.2 g (63%) of substance with m.p. 204° (from dichloroethane), which proved to be identical with the quinoxaline derivative obtained by the counter synthesis from o-carboxybenzil [13] and o-phenylenediamine.

Found %: C 77.11; H 4.20; N 8.67. $C_{21}H_{14}O_2N_2$. Calculated %: C 77.30; H 4.29; N 8.59.

e) Transformation of o-oxalobenzil into benzoin-o-carboxylic acid lactone (XII). One gram of o-oxalobenzil was boiled for 30 minutes with 50 ml of water, and after cooling, the lactone (XII) was filtered. Weight 0.75 g (95%). M.p. 148-149° (from CH_3OH) [7].

Found %: C 75.48; H 4.07. $C_{15}H_{10}O_3$. Calculated %: C 75.63; H 4.20.

The phenylhydrazone of the lactone had m.p. 161° (from alcohol) [7]. The p-nitrophenylhydrazone of the same lactone had m.p. 167° (from CH_3COOH).

Found %: N 10.97. $C_{21}H_{15}O_4N_3$. Calculated %: N 11.26.

3. Transformation of 2-hydroxy-2-phenyl-1,3-indandione (X) into benzoin-o-carboxylic acid lactone (XII). 2-Hydroxy-2-phenyl-1,3-indandione is completely stable when boiled for 30 minutes with water or when treated for 30 minutes at 20° with a 2% methyl alcohol solution of CH_3ONa, but it is transformed into the benzoin-o-carboxylic acid lactone (XII) under the influence of aqueous alkali solutions.

A solution of 0.3 g of 2-hydroxy-2-phenyl-1,3-indandione in 18 ml of 3% KOH solution was boiled in a nitrogen atmosphere for 1 hour, or 0.3 g of the compound in 18 ml of 15% KOH solution was allowed to stand for 15 minutes at 20°.* Then the solution was acidified with H_2SO_4, extracted with ether, the ether solution evaporated, the residual oil boiled with 300 ml of water, and the insoluble tarry residue removed by filtration. On cooling, a precipitate of 0.1 g of lactone (XII) was obtained, m.p. 148-149° (from CH_3OH).

4. Oxidation of 2-(o-tolyl)-3-hydroxy-1,4-naphthoquinone (I; X = $C_6H_4CH_3$-o) with potassium permanganate. To 2.7 g of the quinone [16] in 200 ml of 0.5% KOH solution at 20° and with vigorous stirring was added 2.4 g of $KMnO_4$ in 200 ml of 10% KOH solution. After 1.5 hours 6-8 ml of concentrated $NaHSO_3$ solution was added, the MnO_2 removed by filtration, and the solution made acid with 230 ml of 10% H_2SO_4. The aqueous solution was extracted 5 times with ether, Na_2SO_4 and a small amount of charcoal were added to the ether extract, and after 30 minutes both were removed by filtration. The ether was distilled under slight vacuum at a bath temperature not exceeding 35-40°. The oily residue was extracted 3 times with 5 ml portions of hexane, and then 5 ml of water was added, which initiated rapid crystallization. The precipitate was filtered, washed with a mixture of ether and hexane (1:4), and air-dried for not more than 30 minutes. The obtained triketocarboxylic acid (III; X = $C_6H_4CH_3$-o) melts with decomposition at 59°; yield 2.2 g (62%).

5. Properties and transformations of the triketocarboxylic acid (III; X = o-$C_6H_4CH_3$).

a) The acid crystallizes with 3 molecules of water. Since the acid loses its water of crystallization fairly rapidly in the air and turns into an oily substance, it should be kept under a layer of ether-hexane mixture (1:4), and should be filtered off about 30 minutes prior to analysis. This acid cannot be recrystallized in the normal manner, since it is extremely unstable. When the conditions described in Expt. 4 are observed the acid is obtained in sufficiently pure form.

Found %: C 58.20; H 4.98; H_2O 15.19 (determined by the Fischer method). $C_{17}H_{12}O_5 \cdot 3H_2O$. Calculated %: C 58.03; H 5.14; H_2O 15.43. M (determined by titration) 356; calculated for $C_{16}H_{11}O_3COOH \cdot 3H_2O$ 350. In the titration with HIO_4 the consumption of the latter was 0.95 mole after 4 hours.

b) Transformation into the lactone (IX; R = o-$C_6H_4CH_3$). A solution of 0.5 g of the triketocarboxylic acid in 30 ml of water was boiled for 45 minutes, and after cooling, the lactone precipitate was filtered. Weight 0.35 g (97%); m.p. 103-104° (from CH_3OH).

Found %: C 76.10; H 4.63. $C_{16}H_{12}O_3$. Calculated %: C 76.19; H 4.76.

6. Oxidation of 2-(β-naphthyl)-3-hydroxy-1,4-naphthoquinone (I; X = β-$C_{10}H_7$) with potassium permanganate. To 3 g of the quinone [16] in 200 ml of 0.5% KOH solution at 20° and with vigorous stirring, was added 2.4 g of $KMnO_4$ in 200 ml of 10% KOH solution. After 2 hours the MnO_2 was removed by filtration and the solution was made acid with 230 ml of 10% H_2SO_4. After removing the precipitated naphthoic acid (0.9 g; 52%) by filtration, the mother liquor was extracted 5 times with ether. The ether solution was stirred for 30 minutes with Na_2SO_4 and a small amount of charcoal, the latter were removed by filtration, and the ether was distilled under slight vacuum at a bath temperature not exceeding 35-40°. The rapidly crystallizing residue was filtered. The obtained triketocarboxylic acid (III; X = β-$C_{10}H_7$) was washed 3 times with chloroform. Weight 0.85 g (24%); decomposition point 116°.

7. Properties and transformations of the triketocarboxylic acid (III; X = β-$C_{10}H_7$).

a) The acid crystallizes with 1 molecule of water. It is readily soluble in many organic solvents, moderately soluble in $CHCl_3$, and insoluble in hexane. This acid cannot be recrystallized in the normal manner, since it is extremely unstable. When the conditions described in Expt. 6 are observed, this compound is obtained in fairly pure form.

Found %: C 68.52; H 4.12. $C_{20}H_{12}O_5 \cdot H_2O$. Calculated %: C 68.57; H 4.00. The titration with HIO_4 required 0.99 mole of the latter after 4 hours.

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*The apparatus and operating directions are described in Communication XXII, Expt. 1 [15].

b) Transformation into the lactone (IX; R = β-$C_{10}H_7$). A solution of 0.35 g of the triketocarboxylic acid in 30 ml of water was boiled for 45 minutes, and after cooling, the lactone precipitate was filtered. Weight 0.25 g (87%); m.p. 149° (from CH_3OH).

Found %: C 79.41; H 3.93. $C_{19}H_{12}O_3$. Calculated %: C 79.16; H 4.16.

8. Decarboxylation of triketocarboxylic acids of the (III) type. The decarboxylation reaction was studied under various conditions. The substance samples (0.2-0.3 g) were boiled in either an air or nitrogen atmosphere for 30-45 minutes with either 30-50 ml of water, 2% H_2SO_4 solution, or 2% NaOH solution. When the reaction was run in an atmosphere of air the apparatus and conditions described in Expt. 5b of Communication IV [14] were used, while when the reaction was run in a nitrogen atmosphere an apparatus similar to that described in Expt. 1 of Communication XXII [15] was used. The cleaved carbon dioxide was displaced by either the air or nitrogen and was absorbed in standard alkali solution. The results obtained when the reactions were run in an air atmosphere are summarized in the table. Practically the same values were obtained when the reactions were run in a nitrogen atmosphere. The only exception is the o-pyruvoylphenylglyoxylic acid (III; X = CH_3), which completely failed to decarboxylate when boiled in alkaline solution in the absence of atmospheric oxygen. It should also be mentioned that the triketocarboxylic acid (III; X = $C_6H_4CH_3$-o) shows fairly rapid decarboxylation in the presence of 2% H_2SO_4 even at room temperature.

Starting triketocarboxylic acid (III)	Amount of CO_2 (in %) cleaved during boiling		
	in water	in 2% H_2SO_4	in 2% NaOH
X=CH_3	71.6	74.4	78.1
X=C_6H_5 . . .	96.3	97.3	0
X=$C_6H_4CH_3$-o	98.6	93.7	—
X=β-$C_{10}H_7$ . .	96.1	99.5	0

9. Oxidation of 2-benzyl-3-hydroxy-1,4-naphthoquinone with potassium permanganate. To 2.9 g of the quinone [2,17] in 200 ml of 0.5% KOH solution at 0° and with vigorous stirring, was rapidly added a solution (cooled to 0°) of 2.4 g of $KMnO_4$ in 200 ml of 10% KOH solution. In 1-2 minutes the color of the solution changed from a bright red to a green, and then changed back to a bright red. The MnO_2 precipitate was rapidly filtered, after we had first poured into the receive 230 ml of 10% H_2SO_4 solution cooled to 0°. Filtration of the acid solution gave 2.5 g (89%) of 2-phenyl-3-hydroxy-1,4-naphthoquinone with m.p. 145-146° [12]. The mother liquor was extracted with ether. After distilling off the ether, the residue was recrystallized from 50% alcohol. The yield of o-(β-phenyllactoyl) phenylglyoxylic acid (II; X = $CH_2C_6H_5$) with m.p. 186-187° was 0.1 g (0.3%) (for more details on this acid see Communication XXVII [18]).

SUMMARY

The oxidation of 2-phenyl-, 2-(o-tolyl)- and 2-(β-naphthyl)-3-hydroxy-1,4-naphthoquinone (I) with potassium permanganate under the conditions of the Hooker reaction gave the corresponding triketocarboxylic acids of the (III) type, and the properties and transformations of the latter were studied. The oxidation of 2-benzyl-3-hydroxy-1,4-naphthoquinone under analogous conditions gave o-(β-phenyllactoyl) phenylglyoxylic acid. The fact that these substances were isolated confirms again the validity of our opinions expressed earlier relative to the mechanism of the Hooker reaction.

LITERATURE CITED

[1] S. Hooker, J. Am. Chem. Soc. 58, 1168, 1174, 1179, 1198 (1936).

[2] L. Fieser, J. Hartwell and A. Seligman, J. Am. Chem. Soc. 58, 1223 (1936).

[3] L. Fieser and M. Fieser, J. Am. Chem. Soc. 70, 3215 (1948).

[4] M. M. Shemyakin and L. A. Shchukina, J. Gen. Chem. 18, 1934, 1941 (1948).

[5] L. A. Shchukina, A. P. Kondratyeva and M. M. Shemyakin, J. Gen. Chem. 19, 468 (1949) (T.p. 419).*

[6] L. A. Shchukina, Yu.B. Shvetsov and M.M. Shemyakin, J. Gen. Chem. 21, 346 (1951) (T.p. 381).*

---

*T.p. = C. B. Translation pagination.

[7] G. Vanags and U. Walbe, Ber. 71, 1448 (1938).

[8] S. Gabriel, L. Kornfeld and C. Grunert, Ber. 57, 302 (1924).

[9] R. Mousbacher, J. Am. Chem. Soc. 73, 3245 (1951).

[10] E. Alexander, J. Am. Chem. Soc. 69, 289 (1947); W. Doering, T. Taylor and E. Schoenewaldt, J. Am. Chem. Soc. 70, 455 (1948).

[11] Organic Reactions (Moscow, 1950), II, 106.

[12] L. A. Shchukina and E. P. Semkin, J. Gen. Chem. 26, 1695 (1956) (T.p. 1901).*

[13] S. Gabriel, Ber. 18, 3470 (1885); G. Graebe and P. Juillard, Ber. 21, 2003 (1888).

[14] L. A. Shchukina, A. P. Kondratyeva and M. M. Shemyakin, J. Gen. Chem. 19, 183 (1949) (T.p. 165).*

[15] O. M. Shemyakina, B. M. Bogoslovsky and M. M Shemyakin, J. Gen. Chem. 22, 675 (1952) (T.p. 739).*

[16] O. Neunhoeffer and J. Weise, Ber. 71, 2703 (1938).

[17] L. Fieser, J. Am. Chem. Soc. 48, 3201 (1926).

[18] L. A. Shchukina and M. M. Shemyakin, J. Gen. Chem. 26, 1708 (1956) (T.p. 1915).*

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*T.p. = C. B. Translation pagination.

(4) G. Kresze and [illegible], Ber. [illegible] (19[illegible]).

(5) S. Gabriel, [illegible] and C. [illegible], Ber. 60, [illegible] (19[illegible]).

(6) R. [illegible], J. Am. Chem. Soc. [illegible] (19[illegible]).

(10) E. Alexander, J. Am. Chem. Soc. [illegible] (19[illegible]); W. [illegible], W. Taylor and [illegible], J. Am. Chem. Soc. [illegible] (19[illegible]).

(11) Organic Syntheses, [illegible]

(12) [illegible] and [illegible], Zh. Obshch. Khim. [illegible]

(13) [illegible], Ber. [illegible]; [illegible] and [illegible], Ber. [illegible]

(14) L. A. [illegible] and [illegible]

(15) [illegible]

(16) [illegible] and [illegible], Ber. [illegible]

(17) [illegible], J. Am. Chem. Soc. [illegible]

(18) [illegible] and [illegible], J. Gen. Chem. [illegible]

Received [illegible], 1963 [illegible] Academy of Sciences [illegible]

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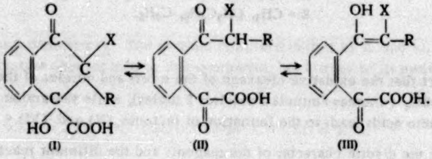
*Tr. = C. S. Translation [illegible]

OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

XXVII. TAUTOMERIC TRANSFORMATIONS AND PROPERTIES OF HYDROXY- AND CHLOROKETOCARBOXYLIC ACIDS

L. A. Shchukina and M. M. Shemyakin

Several years ago we [1-9], and at approximately the same time Fieser [10,11] described a new type of hydroxy- and chloroketocarboxylic acids, showing a tendency for ring-chain tautomerism (I)⇌(II) and for keto-enol transformations (II)⇌(III).



(I) (II) (III)

X = OH and Cl; R = CH_3, C_6H_{11}, $CH_2C_6H_5$, C_6H_5, etc.

According to the data of Fieser, compounds of this type react in most cases in the tautomeric form (I), while on the basis of our data, although at the time quite limited, the impression was gained that either form (II) or (III) usually enters into reaction, but not (I). Later studies of this question, made by us recently on a number of new examples confirmed the validity of our viewpoint.

As study subjects we took the hydroxyketocarboxylic acids and their derivatives with X = OH and R = CH_3, $CH_2C_6H_5$ and C_6H_5, with the result that some of the described compounds are new. The results of these studies and the conclusions derived from them are briefly discussed below.

One of the characteristic properties of the examined hydroxy- and chloroketo acids should be their behavior toward oxidizing agents. In accord with our former observations it was again shown that it is always either form (II) or (III) that is oxidized, but not (I), since, independent of the nature of the oxidizing agent, pH of the medium, temperature and other oxidation conditions, the final products are always o-disubstituted benzene derivatives, and not the corresponding indan derivatives. Thus, the oxidation of the hydroxyketo acids (II; X = OH, R = CH_3 and C_6H_5) in aqueous alkaline solution with either $KMnO_4$ or atmospheric oxygen gave the triketo acids (IV; R = CH_3 and C_6H_5) as the first oxidation products, while the oxidation of the hydroxy- and chloroketo acids (II; X = OH and Cl, R = CH_3 and C_6H_5) with H_2CrO_4 in aqueous H_2SO_4 solution or with $CuSO_4$ in the presence of pyridine gave the corresponding lactones (V; X = Cl, R = CH_3) and (VI; R = CH_3 and C_6H_5).* A similar situation is observed when the hydroxy- and chloroketo acids and some of their derivatives are treated with either aqueous caustic alkali or ammonia solutions; here, the same as in previous cases, only the tautomeric forms (II) or (III) show reaction. Actually, compound (II; X = OH, R = CH_3) when heated with aqueous KOH solution in the absence of atmospheric oxygen is cyclized to 1,2-naphthohydroquinone-4-carboxylic acid [2], while the amide of the chloroketo acid (II; X = Cl, R = CH_3) is converted by the action of concentrated NH_3 to the corresponding lactam (VII; R = CH_3) [8].

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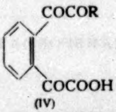
*See [4,9] and the experimental section of the present paper (Expts. 3c and 3d).



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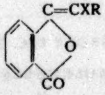

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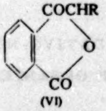

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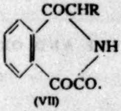
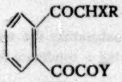


(VII)

Finally, it was shown that the esters of the hydroxyketo acids and the amides of the hydroxy- and chloroketo acids have the structure of (VIII), corresponding to the tautomeric form (II).



(VIII)

X = OH and Cl; Y = OCH_3 and NH_2;
R = CH_3, $CH_2C_6H_5$, C_6H_5.

This follows from the fact that the oxidative cleavage of the esters and amides of the hydroxyketo acids always requires only 1 mole of HIO_4 (whereas Formula I requires 2 moles), while the action of HNO_2 on the amides of the hydroxy- and chloroketo acids leads to the formation of lactones (V) and (VI).*

As a result, despite the diverse character of the reagents and the different reaction conditions employed, our studied hydroxy- and chloroketo acids always reacted only in the tautomeric forms (II) or (III).

In conclusion it is necessary to discuss those data of Fieser [10, 11] that, in his opinion, testify to the ability of the examined types of compounds to react in the bicyclic tautomeric form (I). In the light of what has been said above much of this data is either contradictory or erroneous. Thus, earlier we had shown [9] the lack of agreement between Fieser's spectrographic and chemical studies and the inconclusive nature of his postulations [10] that the esters and acyl derivatives of the hydroxy- and chloroketo acids have the (I) structure. At the present time, this postulation with respect to the esters should be completely rejected, since it is contradicted by the results given above on the titration of this type of compound with HIO_4. Apparently, the statement made by Fieser [11] that he was able to obtain two stereoisomers of the compound (I; X = OH, R = C_6H_{11}) by the oxidation of 2-cyclohexyl-3-hydroxy-1,4-naphthoquinone and 2-cyclohexylindone-3-carboxylic acid also stands in error. This statement is not true for the reason that in both cases the synthesis was run in aqueous alkali medium, i.e. under the conditions where, according to our data, the tautomeric transformations $(I) \rightleftharpoons (II) \rightleftharpoons (III)$ prevail, accompanied by the destruction of either one or both centers of asymmetry.** Of the facts presented by Fieser in support of the tautomeric form (I), only the data relative to the reaction of hydroxyketo acids with 2 moles of HIO_4 [10,11][*] can be considered as having any weight at the present time.

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*See [9] and experimental section of this paper (Expts. 1a, 3b and 4).

**It should be mentioned that an attempt was made by us, under conditions comparable to those recommended by Fieser, to synthesize the two stereoisomers of the compound (I; X = OH, R = C_6H_5). However, when 2-phenyl-3-hydroxy-1,4-naphthoquinone and 2-phenylindone-3-carboxylic acid were treated with H_2O_2 in alkaline medium we obtained the same compound in both cases, in which connection we were able to isolate in the second case the 2-phenylindone-3-carboxylic acid oxide as an intermediate substance; see experimental section, Expts. 2b and 2c.

On the basis of all that has been said above, it must be concluded that in the vast majority of cases the examined hydroxy- and chloroketo acids react in either tautomeric form (II) or (III), but not (I).

EXPERIMENTAL

1. Properties of o-lactoylphenylglyoxylic acid (II; X = OH, R = CH_3) and its derivatives.

a) The data on the reaction with HIO_4 in alcohol solution under the usual conditions are given in Table 1.

TABLE 1

Compound	Literature on the synthesis	Time (in hours)	Consumed HIO_4 (in moles)
Acid (II; X = OH, R = CH_3)	[2,10]	4	1.95
Methyl ester (VIII; X = OH, Y = OCH_3, R = CH_3)	[2,10]	24	1.07
Amide(VIII; X = OH, Y = NH_2, R = CH_3) . . .	[8]	4	1.08
Lactam (VII; R = CH_3)	[8]	4	0.12
Phthalonic acid	[20]	4	0.09

b) Di- and monobenzoyl derivatives. The method described earlier by L. and M. Fieser [10] for the preparation of the dibenzoyl derivative does not lead to this compound, but instead to its pyridine salt with m.p. 180-181° (from CH_3OH).

Found %: C 70.99; H 4.59. $C_{30}H_{23}O_7N$. Calculated %: C 70.73; H 4.52.

To determine the pyridine, the weighed sample of the salt was treated with 5% NaOH solution, and the pyridine was steam-distilled. Its presence in the distillate was qualitatively shown as the picrate (m.p. 165°), while it was determined quantatively to be $(CuPy_2)(SCN)_2$ [19].

Found pyridine in %: 15.20. $C_{25}H_{18}O_7 \cdot C_5H_5N$. Calculated pyridine in %: 15.52.

Treatment of the pyridine salt with hydrochloric acid gave the dibenzoyl derivative with m.p. 193-195° (from 30% C_2H_5OH).

Found %: C 69.58; H 4.03. $C_{25}H_{18}O_7$. Calculated %: C 69.77; H 4.18.

After treatment with 5% KOH solution for 1.5 hours, the dibenzoyl derivative was converted into the monobenzoyl compound with m.p. 184-185° (from CH_3OH).

Found %: C 66.46; H 4.57. $C_{18}H_{14}O_6$. Calculated %: C 66.26; H 4.29.

2. Preparation of o-oxalobenzoin (II; X = OH, R = C_6H_5).

a) From 2-phenyl-1,4-naphthoquinone oxide. A solution of 4 g of the oxide [13] in 2 liters of water was boiled for 72 hours, constantly passing a stream of CO_2-free air through the solution. After cooling, the tarry precipitate was removed by filtration and the solution was evaporated (at 60° and 10 mm) to a volume of 150 ml. Here 0.25 g (6%) of 2-phenyl-3-hydroxy-1,4-naphthoquinone was obtained; m.p. 147° (from CH_3OH) [12]. The mother liquor was extracted 5 times with ether. Removal of the ether gave a yellow oil, which crystallized when rubbed with 2 ml of water and 20 ml of benzene. Weight 1.5 g; m.p. 167-169°. The precipitate was boiled with 1 liter of benzene, while the latter was distilled off to a volume of 0.6 liter. The hot solution was filtered. On cooling, a gelatinous precipitate of the o-oxalobenzoin was obtained. Weight 1.1 g (24%); m.p. 184° (with reddening).

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[*] These data were confirmed by us; see experimental section, Expts. 1a, 3b and 4.

Found %: C 67.44; H 4.45. $C_{16}H_{12}O_5$. Calculated %: C 67.61; H 4.22. M (determined by titration) 291; calculated for $C_{15}H_{11}O_3COOH$ 284. Number of active hydrogen atoms 3.04 (determined by the Terentyev method).

b) From 2-phenyl-3-hydroxy-1,4-naphthoquinone. Five grams of the quinone [12], 50 ml of dioxane and a solution of 2.4 g of soda in 50 ml of water were heated to 70°, the air displaced by nitrogen, 5-8 ml of 25-30% H_2O_2 added, and the heating continued at 70° until the solution turned light yellow (if necessary another 3-5 ml of H_2O_2 added). Then 100 ml of water and 30 ml of 10% H_2SO_4 were added, after which the mixture was filtered and the filtrate extracted 5 times with ether. The isolation and purification of the o-oxalobenzoin was accomplished as described in Expt. 2a. Weight 3.5 g (62%); m.p. 184°.

c) From 2-phenylindone-3-carboxylic acid. To a solution of 3 g of this acid (for its preparation see [12]) in 175 ml of 1.3% NaOH solution in a nitrogen atmosphere at 5-6° was added in 30 minutes 15 ml of 3% H_2O_2. After 10 minutes 30 ml of 10% H_2SO_4 was added and the red tarry precipitate was separated immediately. A pink precipitate soon separated from solution, and was filtered after 30 minutes, recrystallized from 50% CH_3COOH, and then from benzene. The yield of 2-phenylindone-3-carboxylic acid with m.p. 124-125° (decomposition) was 0.8 g (25%).

Found %: C 71.98; H 3.80. $C_{16}H_{10}O_4$. Calculated %: C 72.18; H 3.76. M (determined by titration) 269; calculated for $C_{15}H_9O_2COOH$ 266. The oxide shows oxidative properties. This was determined under the earlier described conditions [13] by heating with KI in CH_3COOH. Found 92.4% iodine.

A solution of 1 g of the oxide in 60 ml of 1.3% NaOH solution was boiled in the apparatus described earlier [14] for 30 minutes in a nitrogen atmosphere. The solution was cooled, acidified with 12 ml of 10% H_2SO_4, and the 2-phenyl-1,3-indandione precipitate filtered; weight 0.5 g (60%); m.p. 146° (from alcohol) [15]. The aqueous mother liquor was extracted with ether. After the ether was distilled off, the residue was purified as described in Expt. 2a. The yield of o-oxalobenzoin with m.p. 184° was 0.4 g (37%).

3. Properties of o-oxalobenzoin (II; X = OH, R = C_6H_5) and its ester.

a) The methyl ester (VIII; X = OH, Y = OCH_3, R = C_6H_5) was obtained by boiling o-oxalobenzoin with CH_3OH in the presence of H_2SO_4 for 8 hours. The product was recrystallized from diisoamyl ether and washed with hexane. M.p. 141-142°.

Found %: C 68.41; H 4.78. $C_{17}H_{14}O_5$. Calculated %: C 68.45; H 4.69.

b) The data on the reaction with HIO_4 in alcohol solution under the usual conditions are given in Table 2.

TABLE 2

Compound	Time (in hours)	Consumed HIO_4 (in moles)
o-Oxalobenzoin	24	2.02
Methyl ester of o-oxalobenzoin	24	1.08

c) Oxidation of o-oxalobenzil (IV; R = C_6H_5). To 1 g of o-oxalobenzoin in 80 ml of 0.5% KOH solution at 8-10° and with vigorous stirring, was added a solution of 0.5 g of $KMnO_4$ in 80 ml of 10% KOH. After 1.5 hours the MnO_2 precipitate was filtered, the solution acidified with 100 ml of 10% H_2SO_4, and then extracted with ether. The ether solution was dried over Na_2SO_4 for 30 minutes, and then the ether was vacuum-distilled to a volume of 2-3 ml at a bath temperature not exceeding 40°. The o-oxalobenzil precipitate was filtered and washed with a small amount of ether. Weight 0.7 g (70%); m.p. 115-116° (with decomposition) [16].

d) Oxidation to o-carboxybenzoin lactone (VI; R = C_6H_5). A mixture of 4.1 g of copper sulfate, 4 g of pyridine and 1.6 ml of water was heated on the water bath until the copper sulfate was completely dissolved, 2.3 g of o-oxalobenzoin was added to the resulting solution, and the heating was continued for 2 hours. The o-carboxybenzoin lactone that separated on cooling was filtered, washed with water, and recrystallized twice from benzene, and then from CH_3OH. Weight 0.5 g (30%); m.p. 149° [16].

e) Oxidation to o-carboxybenzil. A solution of 2 g of o-oxalobenzoin in 0.5 liter of phosphate buffer solution (pH 9.17; capacity 0.15 mole) was boiled for 48 hours with constant passage of a stream of CO_2-free air. After addition of 15 ml of 30% H_2SO_4, the solution was extracted 5 times with ether. The ether solution was dried over Na_2SO_4, and the ether was removed by distillation. The obtained o-carboxybenzil was recrystallized from 30% CH_3COOH. Weight 1.4 g (78%); m.p. 140-141.5° [17].

4. Preparation and Properties of o-(β-phenyllactoyl)-phenylglyoxylic acid (II; X = OH, R = $CH_2C_6H_5$).

The acid was obtained by the oxidation of 2-benzyl-3-hydroxy-1,4-naphthoquinone [18] with H_2O_2, under the conditions of Expt. 2b. The substance crystallizes from 50% alcohol with 1 molecule of water. M.p. 187° (with reddening). Yield 43%.

Found %: C 64.35; H 5.14. $C_{17}H_{14}O_5 \cdot H_2O$. Calculated %: C 64.56; H 5.06. M (determined by titration) 3.09; calculated for $C_{16}H_{13}O_3$ COOH · H_2O 316. When titrated with HIO_4, the consumption of the latter was 1.96 moles after 24 hours.

The methyl ester (VIII; X = OH, Y = OCH_3, R = $CH_2C_6H_5$) was obtained and purified as described in Expt. 3a. M.p. 169-170°.

Found %: C 69.47; H 5.11. $C_{18}H_{16}O_5$. Calculated %: C 69.23; H 5.13. When titrated with HIO_4, the consumption of the latter was 0.91 mole after 24 hours.

SUMMARY

1. It was shown that in the vast majority of cases the hydroxy- and chloroketocarboxylic acids react in either tautomeric form (II) or (III), but not (I).

2. Several new members of the hydroxyketocarboxylic acids and their derivatives were synthesized and their properties studied.

LITERATURE CITED

[1] M. M. Shemyakin and L. A. Shchukina, J. Gen. Chem. 18, 1925 (1948).

[2] L. A. Shchukina, A. P. Kondratyeva and M. M. Shemyakin, J. Gen. Chem. 19, 183 (1949) (T.p. 165).*

[3] L. A. Shchukina and M. M. Shemyakin, J Gen. Chem. 19, 193 (1949) (T.p. 175).*

[4] L. A. Shchukina, A. P. Kondratyeva and M. M. Shemyakin, J. Gen. Chem. 19, 468 (1949) (T.p. 419).*

[5] Yu. B. Shvetsov and M. M Shemyakin, J. Gen. Chem. 19, 480 (1949) (T.p. 431).*

[6] Yu. B. Shvetsov, L. A. Shchukina and M. M. Shemyakin, J. Gen. Chem. 19, 498 (1949) (T.p. 447).*

[7] E. I. Vinogradova, Yu. B. Shvetsov and M. M. Shemyakin, J. Gen. Chem. 19, 507 (1949) (T.p. 457).*

[8] Yu. B. Shvetsov, I. A. Redkin and M. M. Shemyakin, J. Gen. Chem. 21, 339 (1951) (T.p. 373).*

[9] L. A. Shchukina, Yu. B. Shvetsov and M. M. Shemyakin, J. Gen. Chem. 21, 346 (1951) (T.p. 381).*

---

*T.p. = C. B. Translation pagination.

[10] L. F. Fieser and M. Fieser, J. Am. Chem. Soc. 70, 3215 (1948).

[11] L. F. Fieser and A. Bander, J. Am. Chem. Soc. 73, 681 (1951).

[12] L. A. Shchukina and E. P. Semkin, J. Gen. Chem. 26, 1695 (1956) (T. p. 1901).*

[13] L. A. Shchukina, E. I. Vinogradova and M. M. Shemyakin, J. Gen. Chem. 21, 1661 (1951) (T. p. 1823).*

[14] O. M. Shemyakina, B. M. Bogoslovsky and M. M. Shemyakin, J. Gen. Chem. 22, 675 (1952) (T. p. 739).*

[15] F. Nathanson, Ber. 26, 2576 (1893).

[16] L. A. Shchukina, J. Gen. Chem.. 26, 1701 (1956) (T. p. 1907).*

[17] A. Hantzsch and A. Schwiete, Ber. 49, 213 (1916).

[18] L. F. Fieser, J. Am. Chem. Soc. 48, 2930, 3201 (1926); L. F. Fieser, J. Hartwell and A. Seligmann, J. Am. Chem. Soc. 58, 1223 (1936).

[19] H. Meyer, Analysis and Determination of Organic Compounds (Moscow, 1935), II, 399.

[20] C. C. Graebe and F. Trümpy, Ber. 31, 369 (1898); F. Ullmann and J. Uzbachian, Ber. 36, 1805 (1903); J. Braun, Ber. 56, 2333 (1923); R. Fuson, J. Am. Chem. Soc. 48, 1093 (1926).

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SYNTHESIS AND PROPERTIES OF BENZIMIDAZOLE DERIVATIVES

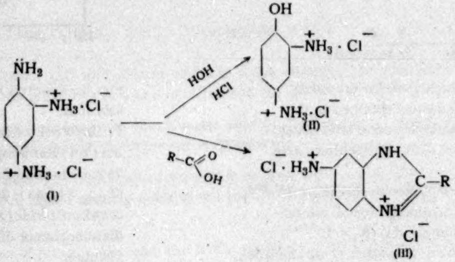
III. THE REACTION OF 1,2,4-TRIAMINOBENZENE WITH CARBOXYLIC ACIDS

G. M. Kharkharova

It is known that the activity of ortho-diamines in their condensation with carboxylic acids in the presence of concentrated HCl is inversely proportional to their basicity constant [1]. 1,2,4-Triaminobenzene [1] does not obey this rule [1]. In our opinion, the reason for its peculiar behavior should be sought in the structure of its hydrochloride. When reacted with mineral acids this amine is capable of forming only the dihydrochloride. The question of which amino group does not participate in the salt formation remains unanswered. However, on the basis of our observations made earlier [2], it can be assumed that due to the ortho-effect (hydrogen bonding), the basicity of the amino groups in the 1,2-positions is reduced, and in the first phase it is the more basic amino group in the 4-position that shows salt formation. In the second phase it is the amino group in the 2-position that enters into salt formation, since the mobility of the free pair of electrons of the amino group in the 1-position is weakened due to the positively charged nitrogen atom found in the paraposition to it. Consequently, it can be assumed that formula (I) reflects the most probable structure of the dihydrochloride, since here the two ($-\overset{+}{N}H_3$) substitutents are situated in the "legitimate", i.e. meta positions with respect to each other. The reason for the inability of 1,2,4-triaminobenzene to form a triacidic salt should be sought in the influence of these two substituents of the second generation on the free amino group.

In support of the proposed structure for the 1,2,4-triaminobenzene salt (I) we cite its transformation, established and described by us below, when heated in dilute hydrochloric acid into 2,4-diaminophenol (II) and the formation of ammonium chloride, similar to the situation that occurs with 2,4-dinitroaniline.

The reaction of the triaminobenzene with carboxylic acids proceeds with highest yield in the presence of 30-35% hydrochloric acid to give mainly 5-amino derivatives of benzimidazole (III).



The yield of the latter drops with decrease in the concentration of hydrogen chloride in the reaction medium. Thus, the condensation of this triaminobenzene, for example, with phenylacetic acid in the presence of 5% hydrochloric acid leads to a highly contaminated product, from which after laborious purification, about 4% of pure

2-benzyl-5-aminobenzimidazole dihydrochloride (III; R = $C_6H_5CH_2$) can be isolated. Here the main reaction product (57-60% yield) proved to be the secondary product (II), isolated by us as silver-gray needles and decomposing at 242-246°. In external appearance, decomposition temperature,* molecular weight, the form of its potentiometric titration curve and its basicity constants** (Fig. 1) the compound resembled the 1,2,4-triaminobenzene dihydrochloride (I). However, when condensed with phenylacetic acid in the presence of 35% hydrochloric acid it did not yield the 2-benzyl-5-aminobenzimidazole hydrochloride (III; R = $C_6H_5CH_2$), which is evidence that it does not contain two amino groups that are ortho with respect to each other. Its nitrogen content was found to correspond to that calculated for the diaminophenol. To elucidate the structure of the secondary product we synthesized the three diaminophenols: 2,4-, 2,5-, and 2,6-which were obtained by the reduction of the corresponding dinitrophenols [3]. The properties of these aminophenols were compared with the properties of our studied substance (see table). It was found that the decomposition points of both the hydrochloride and the picrate of our studied substance coincide with the decomposition points of the dihydrochloride and picrate of 2,4-diaminophenol (II). The mixed melting points of both the picrates and the hydrochlorides were not depressed.

Decomposition Temperatures of the Picrates and Hydrochlorides of the Synthesized Diaminophenols

Diaminophenols	Melting points of the dihydrochlorides	% N (in dihydrochlorides)		Melting points of the picrates
		found	calculated	
2,4-Diaminophenol	242—248°	14.0	14.2	132—136°
2,5-Diaminophenol	195—198	14.5	14.2	184—186
2,6-Diaminophenol	225—230	—	—	Small yield
Product (II)	245—247	14.4, 14.1	14.2	129—131

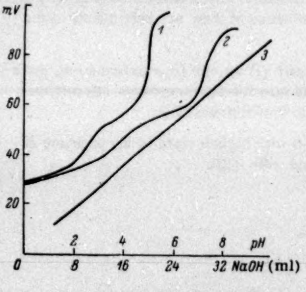


Fig. 1. Potentiometric titration of the secondary product (IV) (2,4-diaminophenol) obtained in the condensation of 1,2,4-triaminobenzene with phenylacetic acid in the presence of 5% hydrochloric acid in tubes under pressure.
1) 1,2,4-triaminobenzene dihydrochloride ($K_1 = 10^{-10.3}$, $K_2 = 10^{-7.9}$, pH 3.0); 2) dihydrochloride of the secondary product (2,4-diaminophenol) ($K_1 = 10^{-10.3}$, $K_2 = 10^{-3.0}$; pH 2.9); 3) characterization of the electrode.

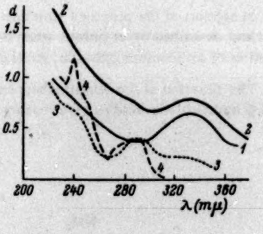


Fig. 2. Spectral curves of the alcohol solutions.
1) dihydrochloride of the secondary product (2,4-diaminophenol) (λ_{max}342mμ), 2) 2,4-diaminophenol dihydrochloride (λ_{max} 342mμ); 3) 2,5-diaminophenol dihydrochloride (λ_{max} 282mμ); 4) 2,6-diaminophenol dihydrochloride (λ_{max} 288mμ).

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*The decomposition point of 1,2,4-triaminobenzene dihydrochloride is 248-250°.

**Replacement of the amino group in the 1-position of 1,2,4-triaminobenzene by a hydroxyl, hardly changes the basicity of the compounds [2] (Fig. 1).

We were able to obtain final proof of the identity of the secondary product isolated from the reaction mixture with the hydrochloride of 2,4-diaminophenol from the ultraviolet spectra (Fig. 2). The maxima of the spectral curves for both products coincided, whereas the maximum for the curve of 2,5-diaminophenol dihydrochloride lies in a different region of the spectrum.

From the above it becomes clear why the dihydrochloride of 1,2,4-triaminobenzene reacts more easily with carboxylic acids in the presence of concentrated hydrochloric acid than does, for example, the dihydrochloride of 3,4-tolylenediamine, where both of the ortho-substituted amino groups participate in the salt formation.

The presence of concentrated (30-35%) hydrochloric acid in the reaction mixture, activating the carboxylic acid, facilitates its condensation with 1,2,4-triaminobenzene, as a result of which the secondary process of desamination proceeds to a lesser degree under these conditions.

EXPERIMENTAL

1,2,4-Triaminobenzene dihydrochloride was obtained in about 70% yield. M.p. 248-250° (decomposition)[1].

Found 0.196 g substance: 20.01 ml 0.1 N NaOH. Calculated: 20 ml 0.1 N NaOH.

The potentiometric titration curve showed two inflection points. pH of the aqueous solution 3.0; $K_1 = 10^{-10.3}$, $K_2 = 10^{-7.9}$ (Fig. 1). The potentiometric titration was run at 25°.

Reaction of 1,2,4-triaminobenzene dihydrochloride with phenylacetic acid in the presence of dilute (5%) hydrochloric acid. A mixture of 5.88 g of 1,2,4-triaminobenzene dihydrochloride, 4.85 g of phenylacetic acid and 30 ml of 5% hydrochloric acid was heated in a sealed glass tube for 5 hours at 150-160°. The tube contents were extracted in the usual manner [1]. From the fractional crystallization we were able to isolate about 0.8 g of ammonium chloride (white powder, subliming at 300° and decomposing with the evolution of ammonia (odor) when treated with aqueous alkali solution) and 0.4-0.5 g (4%) of 2-benzyl-5-aminobenzimidazole dihydrochloride, obtained as gray crystals with decomposition point 280-285°. In its properties this amine corresponded to the one described by us earlier [1]. The mixing of its aqueous solutions with picric acid gave the picrate with m.p. 220-221°. In addition, a secondary product (2,4-diaminophenol) was obtained, which represented the main reaction product (about 60%, based on the amount of 1,2,4-triaminobenzene dihydrochloride taken for reaction). It was isolated as silver-gray needles, decomposing at 245-247°, and quite readily soluble in water and difficultly soluble in 15% hydrochloric acid. Potentiometric titration permitted establishing the presence of two hydrochloric acid molecules per mole of amine in this product (Fig. 1).

Found: 0.298 g substance: 29.1 ml 0.1 N NaOH. $C_6H_8ON_2 \cdot 2HCl$. Calculated: 30.8 ml 0.1 N NaOH.

The potentiometric titration curve of the investigated product had two inflection points (Fig. 1): pH 2.9; $K_1 = 10^{-10.3}$, $K_2 = 10^{-3.0}$, its molecular weight was about 200.

Found %: N 14.4, 14.1. $C_6H_8ON_2 \cdot 2HCl$. Calculated %: N 14.2.

The reaction of product (II) with sodium nitrite in water solution gave a red substance, the water solutions of which did not show the properties of diazo solutions and did not couple with Azotol A.

Product (II) did not condense with phenylacetic acid in the presence of concentrated hydrochloric acid. The starting substance was recovered, decomposing at 220-240°.

The picrate of product (II) was obtained by mixing aqueous solutions of (II) and picric acid, m.p. 129-131° (with decomposition). The mixed melting point of this picrate with the picrate prepared from 2,4-diaminophenol was not depressed.

The spectral curves of product (II), and also of the synthesized 2,4-, 2,5- and 2,6-diaminophenols, were measured on an SF-1 spectrophotometer in alcohol solution (Fig. 2).

SUMMARY

1. The reason for the peculiar behavior shown by 1,2,4-triaminobenzene in its condensation with carboxylic acids in the presence of 30-35% hydrochloric acid should be sought in the structure of its salts.

2. It was postulated and partially proven that it is the 2 and 4 amino groups in 1,2,4-triaminobenzene that participate in salt formation.

3. 1,2,4-Triaminobenzene dihydrochloride is easily converted into the hydrochloride of 2,4-diaminophenol when it is heated with dilute hydrochloric acid in a tube under pressure. The latter also appears as the secondary product in the condensation of 1,2,4-triaminobenzene with phenylacetic acid in the presence of dilute hydrochloric acid.

4. The spectral curves for the hydrochlorides of 2,4-, 2,5- and 2,6-diaminophenols were shown.

LITERATURE CITED

[1] B. A. Porai-Koshits and G. M. Kharkharova, J. Gen. Chem. 24, 1651 (1954) (T.p. 1633).*

[2] G. M. Kharkharova, J. Gen. Chem. Suppl. II, 1663 (1953).

[3] Past and Stuckenberg, Ann. 205, 66 (1880).

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*T.p. = C. B. Translation pagination.

REACTIONS OF HYDRAZINE DERIVATIVES

V. SYNTHESIS OF 3,5,5-TRIALKYLPYRAZOLINES•

A. N. Kost and I. I. Grandberg

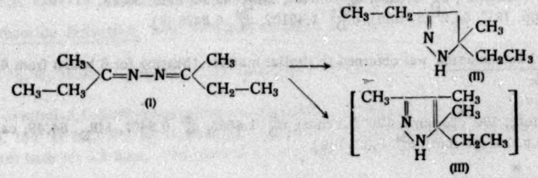
The conversion of acetone azine into 3,5,5-trimethylpyrazoline under the influence of maleic acid was first observed by Curtius [1]. Later certain ketazines were isomerized under the influence of maleic, fumaric and succinic acids or anhydrous hydrogen halides [2-4]. We described [5] a similar reaction of cyclohexanone azine with formic acid to yield 1-formyl-3,4-tetramethylene-5,5-pentamethylenepyrazoline.

Anhydrous formic acid proved to be a good agent for the transformation of the azines of methyl ethyl ketone and methyl propyl ketone into the corresponding N-formylpyrazolines, from which, after hydrolysis with hydrochloric acid, we isolated the free pyrazoline bases. Anhydrous oxalic acid, already used by us earlier [5], also proves to be no less convenient for the isomerization of ketazines. In this case the pyrazoline bases are obtained as the oxalates.

To expand the possibilities of this synthesis we made an attempt to use the mixed azines.

The N. M. Kizhner method [8] does not permit obtaining the hydrazone of cyclohexanone in greater than 20-30% yield, which is also indicated by Perkin [7], for here the main portion of the cyclohexanone is converted into the azine. By modifying the method we were able to increase the yield of the cyclohexanone hydrazone up to 80%. When the hydrazone was reacted under various conditions with carbonyl compounds having a very active carbonyl group (formaldehyde, acetaldehyde) we were unable to isolate appreciable amounts of the mixed azines, since a mixture of symmetrical azines was formed instead. Only with acetone were we able to obtain the mixed azine in 60% yield; (this is easily isomerized with oxalic acid), giving the pyrazoline compound.

The structure of the pyrazolines obtained from azines of symmetrical ketones is not in doubt. As regards the structure of the pyrazolines formed from the azines of unsymmetrical ketones (for example, from methyl ethyl or methyl propyl ketone), then here it depends on which of the hydrogen atoms participated in the reaction. Curtius [3] postulated that it is the methyl group that is involved in the isomerization of methyl ethyl ketone azine (I), that pyrazdine (II) is formed, and not (III), on the basis that the diethyl ketone azine does not react in this sense. N. M. Kizhner [2] proceeded from this postulation, describing the synthesis of 1-methyl-1,2-diethylcyclopropane from methyl ethyl ketone azine (I).



•For Communication IV see Bull. Moscow State Univ.. 1955, No. 12, 119.

To answer this question we reacted hydrazine with 3-methyl-3-hepten-5-one to give pyrazoline (II), identical with the compound obtained from methyl ethyl ketone azine (I). As a result, the postulation made by Curtius proved to be correct. It is interesting to mention that not all ketazines can be converted into pyrazolines. In addition to diethyl ketone azine, mentioned by Curtius [3], we were unable to isomerize the azines of methyl isobutyl ketone and acetophenone (even after long heating with anhydrous oxalic acid). With both oxalic and formic acids the azine of cyclopentanone gives complex condensation products.

EXPERIMENTAL

Cyclohexanone hydrazone hydrate. To a mixture of 104 g (2 moles) of 96% hydrazine hydrate and 250 ml of ether was added dropwise in one hour 96 g (1 mole) of cyclohexanone, with very vigorous stirring. After addition of the ketone the mixture was stirred another 0.5 hour, then, having added 60 ml of methyl alcohol, we heated the mixture to 60° for 1 hour with simultaneous removal of the solvent by distillation; then 80 g of potassium hydroxide and 100 ml of benzene were added and the whole allowed to stand overnight in a separatory funnel. The next day the top benzene layer was separated and vacuum-distilled. The yield of cyclohexanone hydrazone hydrate was 105 g (81.6%).

B.p. 89° (9.5 mm), n_D^{20} 1.5167, d_4^{20} 0.9952.
Literature: B.p. 107-108° (28 mm) [8]; 105-110° (22 mm) [9].

Mixed azine of acetone and cyclohexanone. To 130 g (1 mole) of cyclohexanone hydrazone hydrate at 50° was added in drops 58 g (1 mole) of pure acetone and the whole allowed to stand for 4 hours at 50-55°. Then 20 g of potash and 80 ml of ether were added and after dissolving the potash the ether layer was separated, dried over magnesium sulfate, and vacuum-distilled. The yield of mixed azine of acetone and cyclohexanone was 89 g (59.5%):

B.p. 96-97° (8-9 mm), n_D^{20} 1.4938, d_4^{20} 0.9279, MR_D 47.83; calc. 47.64.
Found %: N 18.52, 18.59. $C_9H_{16}N_2$. Calculated %: N 18.40.

In addition, we obtained 16 g of acetone azine with b.p. 47-55° (52 mm) and 21 g of cyclohexanone azine with b.p. 146-154° (10-12 mm).

Methyl ethyl ketone azine. To 144 g (2 moles) of methyl ethyl ketone was added in drops 52 g (1 mole) of 96% hydrazine hydrate and the mixture heated for 2 hours on the water bath. After addition of 100 ml ether, the azine was salted out by the addition of 50 g of potash. The ether layer was dried over magnesium sulfate and vacuum-distilled. The yield of methyl ethyl ketone azine was 125.5 g (89.5%):

B.p. 108-110° (125 mm). Fraction with b.p. 108.5° (125 mm) has n_D^{20} 1.4540, d_4^{20} 0.8403, MR_D 45.18; calc. 45.12.
Literature: B.p. 168-172°, 85.7° (37 mm), $n_D^{26.6}$ 1.4516, d_0^{24} 0.8335 [9].

Acetone azine was obtained in similar manner from 116 g of acetone, yield 80%:

B.p. 129-132° (753 mm), n_D^{20} 1.4533, d_4^{20} 0.8434, MR_D 35.96; calc. 35.99.
Literature: B.p. 131°; 54.2° (37 mm), $n_D^{24.5}$ 1.45102, d_4^{20} 0.8426 [9].

Methyl propyl ketone azine was obtained in similar manner (heating for 6 hours) from 65 g of the ketone, yield 79.8%:

B.p. 97° (22 mm), 100° (25 mm), 130° (81 mm), n_D^{20} 1.4565, d_4^{20} 0.8401, MR_D 54.49; calc. 54.35.
Literature: B.p. 95° (12 mm), d_4^{24} 0.8330 [9].

3,5,5-Trimethylpyrazoline. To 99 g (1.1 moles) of well-ground anhydrous oxalic acid was added in drops and with stirring, 112 g (1 mole) of acetone azine and the mixture heated on the boiling water bath for 4 hours. The pyrazoline oxalate was decomposed with excess 40% potassium hydroxide solution and extracted

3 times with 50 ml portions of ether. The ether extracts were dried over magnesium sulfate and then vacuum-distilled. The yield of 3,5,5-trimethylpyrazoline was 87.5 g (78%):

B.p. 52.5° (15 mm), n_D^{20} 1.4573, d_4^{20} 0.9025, MR_D 33.86; calc. 33.58.
Literature: B.p. 82° (45 mm), n_D^{20} 1.4566, d_0^{20} 0.8996 [10].

3-Methyl-5,5-pentamethylenepyrazoline was obtained in similar manner from 60 g of the mixed azine of acetone and cyclohexanone, yield 50%:

B.p. 125-132° (21-22 mm); fraction with b.p. 128° (22 mm) has n_D^{20} 1.4975, d_4^{20} 0.9830, MR_D 45.37; calc. 45.23.

Acetyl derivative, m.p. 86° (from 40% alcohol).

Found %: N 14.51, 14.54. $C_{11}H_{18}ON_2$. Calculated %: N 14.42.

5-Methyl-3,5-dipropylpyrazoline from 60 g of methyl propyl ketone azine; yield 63.2%:

B.p. 111.5° (20 mm), 130° (37 mm), n_D^{20} 1.4596, d_4^{20} 0.8867, MR_D 51.93; calc. 52.05.
Found %: N 16.93, 17.01. $C_{10}H_{20}N_2$. Calculated %: N 16.65. Oxalate: M.p. 192° (decomp.) precipitated from alcohol with ether.
Literature: B.p. 101-103° (14 mm), 113-115° (20 mm), n_D 1.4632, d^{18} 0.884 [3].

5-Methyl-3,5-diethylpyrazoline. A mixture of 100 g (0.741 mole) of methyl ethyl ketone azine and 69 g (1.5 moles) of anhydrous formic acid was heated at the boil for 3 hours. Then the mixture was made alkaline with excess concentrated ammonia solution and extracted with 50 ml of ether. The ether extract was dried over magnesium sulfate and then vacuum-distilled. The fraction with b.p. 148-152° (107 mm) was 1-formyl-5-methyl-3,5-diethylpyrazoline; yield 79.7 g (66.4%):

n_D^{20} 1.4860, d_4^{20} 0.9963, MR_D 48.48; calc. 48.61.
Found %: N 16.73, 16.87. $C_9H_{16}ON_2$. Calculated %: N 16.65.

A mixture of 70 g (0.417 mole) of 1-formyl-5-methyl-3,5-diethylpyrazoline and 180 ml of concentrated hydrochloric acid was evaporated in a porcelain dish to 40% of the original volume. Then the residue was made alkaline with concentrated aqueous ammonia solution and extracted 3 times with 50 ml portions of ether. The ether extracts were dried over magnesium sulfate and then vacuum distilled. The yield of 5-methyl-3,5-diethyl-pyrazoline was 42.7 g (73.2%):

B.p. 82.5-83.5° (12 mm), n_D^{20} 1.4622, d_4^{20} 0.9031, MR_D 42.69; calc. 42.81.
Literature: B.p. 78-80° (14 mm), 90-93° (20 mm) [3], 196-197° (754 mm), n_D^{20} 1.4617, d_4^{20} 0.8898 [2], d_4^{18} 0.898 [3].

Oxalate: m.p. 110-112° (from anhydrous alcohol with absolute ether).

N-Phenylcarbamido derivative, m.p. 80° (from alcohol).

Found %: N 16.36, 16.49. $C_{15}H_{21}ON_3$. Calculated %: N 16.21.

The same 5-methyl-3,5-diethylpyrazoline was obtained by heating 63 g (0.5 mole of 3-methyl-3-hepten-5-one (b.p. 164° at 742 mm, n_D^{20} 1.4468, d_4^{20} 0.9097 [11]) with 26 g (0.5 mole) of 96% hydrazine hydrate on the water bath for 0.5 hour. The yield of the pyrazoline was 56.5 g (80.6%):

B.p. 85° (17 mm), n_D^{20} 1.4631, d_4^{20} 0.9022.

N-Phenylcarbamido derivative, m.p. 81°. Does not give a melting point depression when mixed with the specimen described above.

1-Formyl-5-methyl-3,5-dipropylpyrazoline was obtained in similar manner from 40 g of methyl propyl ketone azine. Yield 66.3%:

B.p. 159-161° (32 mm), n_D^{20} 1.4804, d_4^{20} 0.9660, MR_D 57.77; calc. 57.84.
Found %: N 14.38, 14.51. $C_{11}H_{20}ON_2$. Calculated %: N 14.27.

Hydrolysis of 21 g of the formyl derivative gave 5-methyl-3,5-dipropylpyrazoline, yield 90.4%; b.p. 111-113° (19 mm), n_D^{20} 1.4594.

SUMMARY

The rearrangement of ketazines under the influence of anhydrous formic and oxalic acids was studied, leading to the formation of 3,5,5-trialkylpyrazolines.

LITERATURE CITED

[1] T. Curtius and H. Försterling, Ber. 27, 771 (1894).

[2] N. M. Kizhner, J. Russ. Chem. Soc. 44, 179 (1912).

[3] T. Curtius and E. Zinkeisen, J. prakt. Chem. (2), 58, 310 (1898).

[4] A. Franke, Monatsh. 19, 531 (1898); 20, 849 (1899); K. Frey and R. Hoffmann, Monatsh. 22, 760 (1901).

[5] A. N. Kost and I. I. Grandberg, J. Gen. Chem. 25, 2064 (1955) (T.p. 2017).*

[6] S. Tebinov, J. Gen. Chem. 6, 1902 (1936); 7, 654, 656 (1937).

[7] W. Perkin and P. Plant, J. Chem. Soc. 127, 1138 (1925).

[8] N. M. Kizhner and S. Belov, J. Russ. Chem. Soc. 43, 577 (1911).

[9] T. Curtius and K. Thun, J. prakt. Chem. (2), 44, 165 (1891).

[10] N. M. Kizhner, J. Russ. Chem. Soc. 44, 169 (1912).

[11] R. Ya. Levina and N. P. Shusherina, J. Gen. Chem. 20, 868 (1950) (T.p. 903).*

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*T.p. = C. B. Translation pagination.

REDUCTION WITH FORMIC ACID AND ITS DERIVATIVES

V. THE REDUCTION OF QUINOLINIUM SALTS

A. N. Kost and L. G. Yudin

The heating of quinoline with formic acid or, better still, with a mixture of formic acid and sodium formate results in its reduction, giving N-formyl-1,2,3,4-tetrahydroquinoline [1]. It was found that quinolinium salts are reduced in similar manner, but here the reaction does not proceed with pure formic acid (even after heating for many hours), while with catalytic amounts of sodium formate the yields are insignificant; however, if 5 moles of sodium formate and 8 moles of formic acid are used per mole of quinolinium salt, then the yields of N-alkyl-1,2,3,4-tetrahydroquinolines are as high as 80-85%.

However, the use of either sodium or potassium formate requires prolonged heating of the reaction, as a result of which some tarring is observed; consequently, we replaced the sodium formate by triethylamine, which permitted obtaining the N-alkyltetrahydroquinolines in higher yield (up to 93%), shortened the reaction time from 10 to 3-5 hours and, finally, avoided the occurrence of tarring. As in the case of inorganic formates the use of catalytic amounts of triethylamine is not very effective, but its optimum amount is still less than that of a formate (it is sufficient to use 2 moles of triethylamine per mole of quinolinium salt). It should be mentioned that here also a considerable excess (3-4 fold) of formic acid is required for the reduction, as otherwise the yields show considerable reduction. The reaction does not proceed with 85% formic acid. The presence of sulfur compounds does not affect the reduction course.

Due to the large diversity of the data found in the literature [2,3] relative to the constants of N-alkyltetrahydroquinoline derivatives, we ran the counter synthesis of the N-propyl- and N-butyltetrahydroquinolines and obtained constants that agreed with ours and were close to the data of Braun [3]. As regards the data of Torossian [2], who reduced the quinolinium salts with potassium borohydride, apparently they refer to the dihydroquinolines.

EXPERIMENTAL

Quinolinium salts. Methylquinolinium iodide was obtained by reacting methyl iodide with quinoline in the cold. Benzylquinolinium chloride was obtained in a similar manner. The salts from ethyl iodide, ethyl bromide, n-propyl bromide and n-butyl bromide were obtained by heating the respective halides with quinoline on the water bath for 10-20 hours. To remove colored substances, all of the salts were washed with anhydrous acetone and then dried at 80-100°.

N-Propyl-1,2,3,4-tetrahydroquinoline. A mixture of 6.3 g (0.025 mole) of propylquinolinium bromide, 9.2 g (0.2 mole) of anhydrous formic acid and 5 g (0.05 mole) of triethylamine was boiled under reflux for 5 hours. The cooled mixture was then made alkaline, the top layer separated, and the water layer extracted 3 times with ether, adding the extract to the top layer. On drying this over fused caustic and distilling, we obtained 4.0 g (93%) of N-propyl-1,2,3,4-tetrahydroquinoline:

B.p. 141-143° (15 mm), n_D^{20} 1.5575.
Hydrochloride: M.p. 162° (from alcohol); picrate m.p. 93.5° (from alcohol).
Found %: C 53.31, 53.46; H 5.02, 5.14; N 13.65, 13.76. $C_{18}H_{20}O_7N_4$. Calculated %: C 53.46; H 4.98; N 13.85.

The same substance was obtained by the 20-hour boiling of propyl bromide with 1,2,3,4-tetrahydroquinoline in the presence of soda and had the constants: b.p. 130-132° (10 mm), n_D^{20} 1.5583.

Picrate, m.p. 93.5° (from alcohol). The mixed melting point of the picrates was not depressed.

Literature: B.p. 146° (16 mm); picrate m.p. 73° [3], 178° [2]; hydrochloride m.p. 162° [3].

N-Butyl-1,2,3,4-tetrahydroquinoline. To a solution of 13.3 g (0.05 mole) of butylquinolinium bromide in 18.4 g (0.4 mole) of anhydrous formic acid was added 17 g (0.28 mole) of sodium formate and the mixture heated in an oil bath under reflux for 10 hours with periodic shaking (here the sodium formate crystallized on the sides of the flask). Then the cooled reaction was diluted with water (to dissolve the sodium formate), made strongly alkaline, the oil layer separated, and the aqueous layer extracted several times with ether. The ether extracts were combined with the main layer, dried over alkali, and distilled. The yield of N-butyl-1,2,3,4-tetrahydroquinoline was 7.6 g (80%):

B.p. 137-139° (6-7 mm), n_D^{20} 1.5518.
Picrate m.p. 93-94° (from alcohol).
Found %: C 54.83, 54.85; H 5.31, 5.53. $C_{19}H_{22}O_7N_4$. Calculated %: C 54.54; H 5.30.

The reduction of butylquinolinium bromide with triethylamine formate gave an 85% yield. The same substance was obtained by long heating of butyl bromide with tetrahydroquinoline in the presence of soda and had m.p. 131-135° (4 mm), n_D^{20} 1.5510; picrate, m.p. 93.5° (from alcohol). The mixed melting point of the picrates was not depressed.

Literature: B.p. 141-145° (10 mm); picrate m.p. 195° [2].

N-Methyl-1,2,3,4-tetrahydroquinoline (Kairoline) was obtained by the reduction of methylquinolinium iodide in the presence of triethylamine. Yield 50%.

B.p. 115-118° (11 mm), n_D^{20} 1.5800. Methiodide m.p. 174°; picrate m.p. 125° (from alcohol).
Found %: C 50.90, 51.04; H 4.34, 4.35; N 14.52, 14.81. $C_{16}H_{16}O_7N_4$. Calculated %: C 51.06; H 4.28; N 14.88. Literature: b.p. 241-243° [4]; picrate m.p. 122° [5], 125° [4]; methiodide m.p. 172-174° [6].

N-Ethyl-1,2,3,4-tetrahydroquinoline was obtained in a similar manner from ethylquinolinium bromide. Yield 87.5%.

B.p. 135-137° (16 mm), n_D^{20} 1.5660. Picrate m.p. 118°.
Found %: C 52.41, 52.53; H 4.75, 4.88. $C_{17}H_{18}O_7N_4$. Calculated %: C 52.30; H 4.64.
Literature: B.p. 115° (8.5 mm); picrate m.p. 117-118.5° [7].

N-Benzyl-1,2,3,4-tetrahydroquinoline. From benzylquinolinium chloride (with triethylamine). Yield 83.6%.

B.p. 178-180° (4 mm), m.p. 36°. Picrate m.p. 95°.
Literature: B.p. 218-222° (38 mm), m.p. 36-37° [8].

SUMMARY

The reduction of quinolinium salts by treatment with formic acid in the presence of either sodium formate or triethylamine was described.

LITERATURE CITED

[1] A. N. Kost and L. G. Yudin, J. Gen. Chem. 25, 1947 (1955) (T.p. 1891).*

[2] R. Torossian, Compt. rend. 235, 1312 (1952).

---

*T.p. = C. B. Translation pagination.

[3] J. Braun, Ber. 42, 2222 (1909).

[4] A. Ladenburg, Ber. 28, 1171 (1895).

[5] E. Spath and A. Kolbe, Monatsh. 43, 469 (1922).

[6] L. Knorr, Ber. 32, 732 (1899).

[7] J. Dodonoff, J. prakt. Chem. (2), 117, 156 (1927).

[8] E. Wedekind, Ber. 35, 125 (1902).

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Moscow State University

IMIDAZOLE SERIES

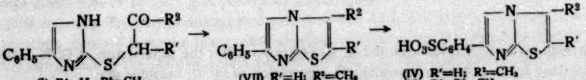
IV. REACTION OF SULFURIC ACID WITH 2-β-KETOALKYL(ARYL)-MERCAPTOIMIDAZOLES

P. M. Kochergin and M. N. Shchukina

It was shown in the previous communication [1] that the heating of certain 2-β-ketoalkylmercaptoimidazoles with hydrochloric acid,or the boiling of their hydrochlorides in butyl alcohol results in their cyclization to imidazo-(2, 1-b)-thiazole derivatives. It was desirable to study the reaction of sulfuric acid with these compounds, since it is indicated [2] in the literature that the heating of 4(5)-methyl-2-acetonylmercaptoimidazole to 100° with concentrated sulfuric acid results in its cyclization to a bicyclic compound, which, in our opinion, is not 3,5-dimethylimidazo-(2-1-b)-thiazole, as the authors believe, but instead is 3,6-dimethylimidazo-(2,2-b)-thiazole.

In this paper we studied the reaction of concentrated sulfuric acid with our earlier synthesized 4(5)-phenyl-2-β-ketoalkyl(aryl)-mercaptoimidazoles [1] and established that these compounds under the influence of sulfuric acid are also capable of cleaving a molecule of water with the formation of imidazo-(2,1-b)-thiazole derivatives. If the radicals linked to the sulfur are either aliphatic or alicyclic ketone rests, then closure of the thiazole ring proceeds even at room temperature. For example, the treatment of 4(5)-phenyl-2-acetonylmercaptoimidazole with 95% sulfuric acid(letting it stand for several hours) and subsequent working up of the reaction mixture gave, in addition to the starting substance, 3-methyl-6-phenylimidazo-(2,1-b)-thiazole (I) in 12-13% yield. At 30-45° the cyclization of 2-β-ketoalkylmercaptoimidazoles proceeds very easily and in excellent yield (92-97%) to the corresponding cyclic compounds. We obtained by this method the earlier described [1] 3-methyl-6-phenylimidazo-(2,1-b)-thiazole (VII), 2,3-dimethyl-6-phenylimidazo-(2,1-b)-thiazole (VIII) and 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole (IX). However, the S-derivatives of 4(5)-phenyl-2-mercaptoimidazole with aliphatic aromatic ketone rests fail to cyclize under these conditions. For example, the treatment of 4(5)-phenyl-2-p-nitrophenacylmetcaptoimidazole (for 12 hours at room temperature) and of 4(5)-phenyl-2-m-nitrophenacylmercaptoimidazole (for 2.5 hours at 40-45°) with 95.6% sulfuric acid and subsequent working up of the solutions gave only the starting substances. The reaction of sulfuric acid with 4(5)-phenyl-2-β-ketoarylmercaptoimidazoles was not studied at higher temperatures, since under these conditions, as will be shown below, it is possible to sulfonate the benzene rings of the formed 3,6-diarylimidazo-(2,1-b)-thiazoles.

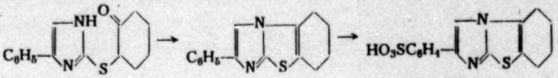
When concentrated sulfuric acid is reacted with 4(5)-phenyl-2-β-ketoalkylmercaptoimidazoles (or their hydrohalide salts) at 95-100° there occurs not only cyclization with the formation of 6-phenylimidazo-(2,1-b)-thiazoles or of 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole (in the case of 4(5)-phenyl-2-(2'-cyclohexanonyl)-mercaptoimidazole), but also sulfonation of the latter; here either 6-p-sulfophenylimidazo-(2,1-b)-thiazoles or 10-p-sulfophenylimidazo-(2,1-b)-tetrahydrobenzothiazole are formed. Thus, the heating of the S-acetonyl-(I), methylacetonyl-(II) and cyclohexanonyl-(III) derivatives of 4(5)-phenyl-2-mercaptoimidazole with 95.6% sulfuric acid gave the sulfo acids (IV), (V) and (VI) in 73-93% yield.



(I) $R'=H$; $R^2=CH_3$
(II) $R'=R^2=CH_3$

(VII) $R'=H$; $R^2=CH_3$
(VIII) $R'=R^2=CH_3$

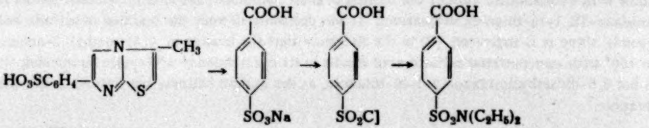
(IV) $R'=H$; $R^2=CH_3$
(V) $R'=R^2=CH_3$



(III) (IX) (VI)

Consequently, the benzene ring, attached either to the 6 position of the imidazo-(2,1-b)-thiazole bicycle or the 10 position of the imidazo-(2,1-b)-tetrahydrobenzothiazole tricycle, acquires the ability to be very easily sulfonated. The same sulfo acids are also formed when the 6-phenylimidazo-(2,1-b)-thiazoles and 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole (or their hydrohalide salts) are reacted directly with sulfuric acid. The sodium salts of the two sulfo acids (IV) and (VI) were prepared, which, in contrast to the salts of p-sulfobenzoic acid [3,4], easily regenerated the free sulfo acids when treated with hydrochloric acid.

The structure of 3-methyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole (IV) as shown by its oxidation with potassium permanganate in alkaline solution, where the sodium salt of p-sulfobenzoic acid [3,4] was obtained. Treatment of this salt with chlorosulfonic acid converted it into p-chlorosulfonylbenzoic acid [4], the treatment of which with diethylamine gave a substance that was identical with the p-N,N-diethylsulfonamidobenzoic acid [5] synthesized from p-toluenesulfonyl chloride.



(IV)

The structures of the other sulfo acids (V) and (VI) were not determined by us, although by analogy with (IV), it can be assumed that in these compounds also the sulfo group occupies the para-position of the benzene ring. All of the obtained compounds, with the exception of (VII), (VIII) and (IX), the action of which had already been mentioned [1], were tested in the chemotherapeutical section of the All-Union Scientific Research Institute of Pharmaceutical Chemistry for their antibacterial activity (spectrum of 16 types of microbes).* The hydrochloride of 3-methyl-6-phenylimidazo-(2,1-b)-thiazole and the sodium salt of 3-methyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole were also tested pharmacologically.** These compounds do not show a high activity.

EXPERIMENTAL

3-Methyl-6-phenylimidazo-(2,1-b)-thiazole.(VII). A solution of 1 g of 4(5)-phenyl-2-acetonylmercaptoimidazole (I) in 5 ml of 95% sulfuric acid was heated on the water bath at 40-42° for an hour, after which it was poured into 20 ml of cold water, the resulting precipitate filtered, washed with acetone, then with ether, and dried. The yield of 3-methyl-6-phenylimidazo-(2,1-b)-thiazole sulfate with m.p. 197-200° was 1.3 g (97%), colorless prisms after recrystallization from alcohol with m.p. 217-218°, and difficultly soluble in water and alcohol.

Found %: N 8.76. $C_{12}H_{12}O_4N_2S_2$. Calculated %: N 8.97.

Decomposition of the sulfate in sodium acetate solution gave the base, 3-methyl-6-phenylimidazo-(2,1-b)-thiazole, as colorless prisms (from alcohol) with m.p. 113-113.5°. Its mixed melting point with the original substance (m.p. 120-121°) was 80-83°. The hydrochloride was obtained as colorless needles from alcohol with m.p. 228-232° (decomposition).

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*The testing was done by S. N. Milovanova and A. A. Mikerina under the supervision of G. N. Pershin.

**The testing was done by S. S. Liberman under the supervision of M D. Mashkovsky.

2,3-Dimethyl-6-phenylimidazo-(2,1-b)-thiazole (VIII). A solution of 0.35 g of 4(5)-phenyl-2-(α-methylacetonyl)-mercaptoimidazole (II) in 4 ml of 95.6% sulfuric acid was heated at 30-35° for an hour, after which it was poured into 10-12 ml of cold water and neutralized with sodium hydroxide solution. The obtained precipitate was filtered, washed with water, and dried. The yield of 2,3-dimethyl-6-phenylimidazo-(2,1-b)-thiazole with m.p. 147-150° was 0.315 g (98.2%), after recrystallization from alcohol – colorless plates with m.p. 157-158°. Its mixed melting point with the original substance (m.p. 96-97°) was 80-83°.

10-Phenylimidazo-(2,1-b)-tetrahydrobenzothiazole (IX). A solution of 2.7 g of 4(5)-phenyl-2-(2'-cyclohexanonyl)-mercaptoimidazole (III) in 11 ml of 95% sulfuric acid was allowed to stand at room temperature for 30 minutes, after which it was heated on the water bath at 45-50° for 20 minutes and then poured into 25-30 ml of cold water. The resulting white crystalline precipitate was filtered, washed with water, acetone, ether, and dried. The yield of 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole sulfate with m.p. 228-230° was 3.3 g. Recrystallization from alcohol gave colorless tetragonal plates with m.p. 232-234°, difficultly soluble in water and alcohol.

Found %: N 8.19. $C_{15}H_{16}O_4N_2S_2$. Calculated %: N 7.95.

Decomposition of the sulfate in aqueous sodium bicarbonate solution gave the 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole with m.p. 168-169°, after recrystallization from alcohol – colorless needles with m.p. 169°. Neutralization of the aqueous sulfuric acid mother liquor with potassium carbonate gave another 0.2 g of substance with m.p. 164-165°, the melting point of which was not lowered when the substance was mixed with 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole. Total yield 92%).

3-Methyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole (IV).

a) A solution of 2.3 g of 4(5)-phenyl-2-acetonylmercaptoimidazole (I) in 15 ml of 95.6% sulfuric acid was heated on the boiling water bath for 30 minutes, after which it was cooled and poured into 50-60 ml of cold water. The resulting white crystalline precipitate was filtered, washed with a small amount of cold water, and dried. The yield of 3-methyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole was 2.2 g (73.3%). Slender colorless needles (from water), failing to melt at 360°, insoluble in organic solvents and mineral acids, difficultly soluble in water, and readily soluble in sodium bicarbonate solution. Crystallizes with a half-molecule of crystallization water.

Found %: C 47.66; H 3.65; N 8.90; S 21.02; H_2O 2.24. M 295.86. $C_{12}H_{10}O_3N_2S_2 \cdot 0.5H_2O$. Calculated %: C 47.49; H 3.65; N 9.23; S 21.11; H_2O 2.63. M 303.20.

b) A solution of 4.4 g of 3-methyl-6-phenylimidazo-(2,1-b)-thiazole hydrochloride in 25 ml of 95.6% sulfuric acid was heated on the boiling water bath for 30 minutes, and then was worked up the same as in the preceding experiment. The yield of 3-methyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole was 4 g (74%).

Sodium salt of 3-methyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole. To a solution of 0.56 g of sodium bicarbonate in 10 ml of water was added 2.05 g of 3-methyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole, in which connection carbon dioxide was evolved. The solution was filtered and poured into 150 ml of anhydrous acetone; the resulting white crystalline precipitate was filtered, washed with anhydrous acetone, and dried. The yield of 3-methyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole sodium salt was 1.65 g. The addition of hydrochloric acid to the mother liquor gave 0.4 g of starting sulfo acid. The sodium salt of 3-methyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole was obtained as colorless crystals, readily soluble in water and alcohol, difficultly soluble in acetone, and insoluble in organic solvents; hydrochloric acid decomposes the salt to give the corresponding sulfo acid.

Proof of the 3-methyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole structure. a) To a boiling solution of 4 g of 3-methyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole in 50 ml of 8% aqueous sodium hydroxide solution was added in drops a solution of 16-16.5 g of potassium permanganate in 200-220 ml of water until decolorization ceased (the excess potassium permanganate was decolorized by the addition of several drops of methyl alcohol). The solution, filtered from the manganese dioxide, was evaporated in vacuo to dryness, concentrated hydrochloric acid was added to the residue (until acid to Congo), and the obtained precipitate was filtered and dried. The yield of halogen-free substance was 1.7 g. Evaporation of the mother liquor to a volume of 30 ml and subsequent cooling of the solution gave another gram of the same substance. The total yield of monosodium p-sulfobenzoate was 2.7 g (96.1%). Elongated colorless prisms (from water) or square plates (from saturated sodium chloride solution).

Found M 215.3. $C_7H_5O_5SNa$. Calculated M 224.08.

b) To 1.87 g of sodium p-sulfobenzoate, obtained as described above and vacuum dried at 130° over phosphorous pentoxide, was cautiously added 2.9 ml of chlorosulfonic acid, after which the mixture was heated for 70 minutes at 100-104°. The dark brown solution was cooled and poured over 20-25 g of ice; the resulting white precipitate was filtered, washed with a small amount of cold water, and dried in a vacuum desiccator. The yield of substance with m.p. 202-205° (decomposition) was 1.15 g (62.5%). Its mixed melting point with p-chlorosulfonylbenzoic acid[4] [m.p. 232-235° (decomposition)] was 203-207° (decomp.).

c) A solution of 1 g of this substance in 9 ml of acetone was heated with activated charcoal, filtered, and added in drops with stirring to a solution of 1 g of diethylamine in 5 ml of water at -2 to 0°, after which the reaction mixture was stirred at room temperature for 30 minutes. Then the solvent was vacuum distilled, and the residue was treated with 20% sulfuric acid until acid to Congo. A light yellow crystalline precipitate separated on cooling, then was filtered, washed with cold water, and dried. The yield of substance with m.p. 189-192° was 1.03 g (88.8%), after recrystallization from alcohol – light yellow crystals with m.p. 192-194°. Its mixed melting point with p-N,N-diethylsulfonamidobenzoic acid [5] (m.p. 192-194°) was 192-194°.

2,3-Dimethyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole (V). A solution of 0.45 g of 4(5)-phenyl-2-(α-methylacetonyl)-mercaptoimidazole (II) in 4 ml of 95.6% sulfuric acid was heated on the boiling water bath for 30 minutes. Then the same treatment as was used to obtain (IV) gave 0.4 g (81.5%) of 2,3-dimethyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole. Slender colorless needles from water, remaining solid at 360°, and having the same solubility as substance (IV).

Found %: C 50.65; H 3.98; N 9.30; S 20.60. $C_{13}H_{12}O_3N_2S_2$. Calculated %: C 50.61; H 3.92; N 9.08; S 20.83.

10-p-Sulfophenylimidazo-(2,1-b)-tetrahydrobenzothiazole (VI).

a) A solution of 1 g of 4(5)-phenyl-2-(2'-cyclohexanonyl)-mercaptoimidazole (III) in 7 ml of 95.6% sulfuric acid was heated on the boiling water bath for 30 minutes, after which it was worked up by the technique used to obtain (IV). The yield of 10-p-sulfophenylimidazo-(2,1-b)-tetrahydrobenzothiazole was 1.15 g (93.5%). Colorless needles from water, remaining solid at 360°, and having the same solubility as substance (IV).

Found %: C 52.83; H 4.27; N 8.50; S 19.02. $C_{15}H_{14}O_3N_2S_2$. Calculated %: C 53.86; H 4.22; N 8.38; S 19.18.

b) A solution of 0.44 g of 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole in 4 ml of 95.6% sulfuric acid was heated on the boiling water bath for 30 minutes, after which it was worked up the same as in the preceding experiment. The yield of 10-p-sulfophenylimidazo-(2,1-b)-tetrahydrobenzothiazole was 0.56 g (96.9%).

Sodium salt of 10-phenylimidazo-(2,1-b)-tetrahydrobenzothiazole. To a solution of 0.1 g of sodium bicarbonate in 10 ml of water was added 0.4 g of 10-p-sulfophenylimidazo-(2,1-b)-tetrahydrobenzothiazole, in which connection carbon dioxide was evolved. The solution was filtered and worked up by the same technique that was used to obtain the sodium salt of 3-methyl-6-p-sulfophenylimidazo-(2, 1-b)-thiazole. The yield of 10-p-sulfophenylimidazo-(2,1-b)-tetrahydrobenzothiazole sodium salt was 0.2 g. Colorless crystals, soluble in water and alcohol, difficultly soluble in acetone, and insoluble in most of the other organic solvents; hydrochloric acid decomposes the salt to give the corresponding sulfo acid.

SUMMARY

1. It was established that the reaction of concentrated sulfuric acid with 4(5)-phenyl-2-δ-ketoalkylmercaptoimidazoles at 30-45° results in the cleavage of a molecule of water, in which connection imidazo-(2,1-b)-thiazole derivatives are formed; 4(5)-phenyl-2-δ-ketoarylmercaptoimidazoles fail to cyclize under these conditions.

2. Not only closure of the thiazole ring, but also sulfonation of the benzene ring occurs when 4(5)-phenyl-2-β-ketoalkylmercaptoimidazoles are reacted with concentrated sulfuric acid at 95-100°, and here 6-sulfophenylimidazo-(2,1-b)-thiazoles are formed, while in the case of 4(5)-phenyl-2-(2'-cyclohexanonyl)-mercaptoimidazole, the 10-sulfophenylimidazo-(2,1-b)-tetrahydrobenzothiazole is formed.

3. The structure of 3-methyl-6-p-sulfophenylimidazo-(2,1-b)-thiazole was shown and a theory was expressed relative to the structure of the other obtained sulfo acids.

LITERATURE CITED

[1] P. M. Kochergin and M. N. Shchukina, J. Gen. Chem. 26, 458 (1956) (T.p. 483).*

[2] H. Andersag and K. Westphal, Ber. 70, 2035 (1937).

[3] J. Remsen, Ann. 178, 286 (1895).

[4] S. Smiles and D. G. Harrison, J. Chem. Soc. 121, 2022 (1922).

[5] T. P. Sycheva, N. V. Savitskaya and M. N. Shchukina, J. Gen. Chem. Suppl. I, 568 (1953).

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*T.p. = C. B. Translation pagination.

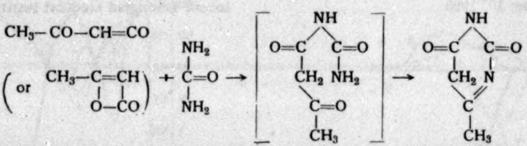
PREPARATION OF 4-METHYLURACIL BASED ON DIKETENE

N. V. Khromov-Borisov and R. S. Karlinskaya

As early as 1948 it was decided by the Pharmacological Committee of the Scientific Council of the Ministry of Health of the Russian Soviet Federative Socialist Republic to use 4-methyluracil (metacil) (I) in the treatment of leucopenic diseases. At the present time the use of 4-methyluracil is being expanded. In addition, 4-methyluracil serves as the starting substance for the synthesis of a new medicinal – pentoxyl. Under the influence of pentoxyl a marked increase in the number of white corpuscles is observed for patients suffering from various forms of leucopenia. Pentoxyl is extremely effective in the treatment of agranulocytic angina of unknown origin, and also of leucopenic diseases caused by chemical (benzene, sulfanilamides, pyramidon, etc.) and physical (x-rays, radium) agents [1, 2].

In recent years the problem of finding a convenient method for the preparation of 4-methyluracil has constantly increased in importance. Until recently only one practical method existed for the preparation of 4-methyluracil: the condensation of urea with acetoacetic ester [3]. This synthesis takes several days; the yield of 4-methyluracil is 50-60%.

We undertook the task of developing a method for the synthesis of 4-methyluracil from diketene and urea by the following scheme:



(I)

According to patent data [4], 4-methyluracil can be obtained by heating a mixture of equimolar amounts of urea and diketene in dioxane.

A repetition of the patent revealed that here 4-methyluracil is obtained in 12% yield, and only when operating in pure, well-dried dioxane.

In the process of finding a rational method for the preparation of 4-methyluracil from diketene and urea, we found that the most suitable medium for this reaction is chlorobenzene as the solvent and pyridine as the catalyst.

When the necessary conditions are observed (see experimental section), the reaction of equimolar amounts of diketene and urea gave 4-methyluracil in 64-65% yield, in which connection the reaction required approximately 1 hour.

It should be mentioned that when the reaction is run in the absence of pyridine the yield of 4-methyluracil dropped to 35-38%; if the reaction is run in pyridine solution, then, in general, 4-methyluracil is not formed.

EXPERIMENTAL

Condensation of urea with diketene in chlorobenzene medium in the presence of pyridine. A mixture of 46 ml of diketene (concentration 92%), 31.6 g of urea and 250 ml of chlorobenzene was heated to 80° and to the obtained urea suspension was added, with good mixing, 2 ml of pyridine (after the heat was turned off). The formation of 4-methyluracil began within several minutes, accompanied by considerable heat evolution.

The temperature was not permitted to rise above 125°, in which connection external cooling with water was applied when necessary. After 50 minutes the mixture was cooled, the 4-methyluracil precipitate filtered, washed successively with pure chlorobenzene, alcohol and water, and dried. Yield 41.7-42.3 g (64-65%).

Using the method described in the patent [4], the reaction of 6 g of urea with 9 ml of diketene in 30 ml of dioxane gave 1.6 g (12%) of 4-methyluracil.

SUMMARY

1. A method was developed for the preparation of 4-methyluracil from diketene and urea in chlorobenzene medium and using pyridine as the catalyst.

2. It was established that the preparation method developed by us has a number of advantages over the method used at the present time to obtain 4-methyluracil from acetoacetic ester and urea.

LITERATURE CITED

[1] N. V. Lazarev and G. I. Felistovich, Pentoxyl and Its Use in Aleucemic Diseases (Navy Medical Academy Press, 1953).

[2] N. V. Khromov-Borisov and R. S. Karlinskaya, Med. Ind. USSR 1955, 127.

[3] Organic Syntheses (1949), Symposium Volume II, 335.

[4] U.S. Patents 2,138,756 (1938) and 2,174,239 (1939).

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ABSORPTION SPECTRA OF TRIPHENYLAMINE AND ITS p-NITRO DERIVATIVES IN PURE ALCOHOL SOLUTION AND IN THE PRESENCE OF SODIUM ALCOHOLATE. I

P. M. Bugai

To study the interrelationship between color and structure of p-nitro derivatives of triphenylamine as a function of the medium, we examined the absorption spectra of these substances in ethanol, and in ethanol in the presence of sodium alcoholate.

We synthesized the studied p-nitro derivatives of triphenylamine by our earlier developed method [1]. All of the obtained substances and necessary solvents were purified to spectroscopic quality. The studies were made with a spectrograph of the ISP-22 type and then were checked with an SF-4 spectrophotometer. The study results with both instruments gave nearly complete agreement of the absorption bands at the maxima.

The absorption spectra of triphenylamine, 4-nitrotriphenylamine, 4,4'-dinitrotriphenylamine and 4,4',4''-trinitrotriphenylamine were taken in pure ethanol.

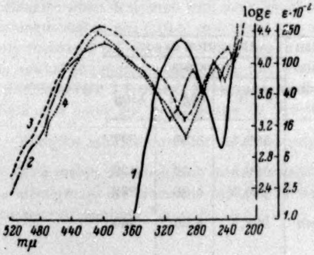


Fig. 1. Absorption spectra curves in ethanol solution.
1) triphenylamine, 2) 4'-nitrotriphenylamine, 3) 4,4'-dinitrotriphenylamine, 4) 4,4',4"-trinitrotriphenylamine.

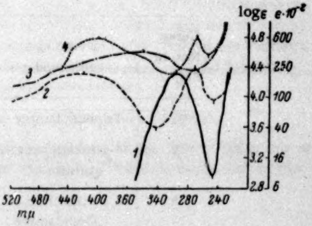


Fig. 2. Absorption spectra curves in ethanol in the presence of 2 moles of sodium alcoholate.
1) triphenylamine, 2) 4'-nitrotriphenylamine, 3) 4,4'-dinitrotriphenylamine, 4) 4,4',4"-trinitrotriphenylamine.

The absorption spectra of the first three compounds in ethanol solution had been taken earlier by other investigators [2] using a spectrophotometer, while the absorption spectrum of triphenylamine alone had been taken even much earlier [3].

It should be mentioned that our data show good agreement with those given in the literature for the bands with absorption maxima in ethanol solutions.

The spectral curves in ethanol for the p-nitro derivatives of triphenylamine are shown in Fig. 1 and compared with the curve for triphenylamine itself. The color of all of the studied substances remained practically unchanged in ethanol solution, i.e. it remained characteristic for the crystalline forms.

This is explained by the fact that for all of the substances the absorption bands in the visible region are found in one wavelength interval. Only solvation of the compounds occurs in an alcoholic polar solvent, and consequently the color of the solutions fails to change here.

TABLE 1

Curve Nos. in Fig. 1	Name of compound	Color of solution in ethanol	Absorption bands maxima		
			$\epsilon \cdot 10^{-2}$	log ϵ	λ mμ
1	Triphenylamine	Colorless	199.5	4.30	297
2	4-Nitrotriphenylamine	Yellow	182.0 77.6 100.0	4.26 3.89 4.00	397 282 254
3	4,4'-Dinitrotriphenylamine	Yellow	309.0 154.9	4.49 4.19	403 235
4	4,4',4"-Trinitrotriphenylamine	Yellow	240.0 91.2	4.38 3.96	405 250

Absorption spectra of p-nitro derivatives of triphenylamine in ethanol in the presence of sodium alcoholate. To determine the reasons for the formation of color shown by nitro derivatives of triphenylamine in the presence of 2 moles of sodium alcoholate in ethanol solution, we made a spectrographic study of the same substances whose spectra were taken in pure ethanol solution.

The absorption spectra curves of all of the substances are shown in Fig. 2, in which connection the curves were obtained at low solution concentrations ($1 \cdot 10^{-3}$ and $1 \cdot 10^{-4}$ M).

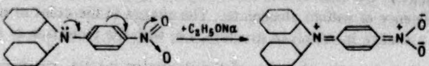
TABLE 2

Curve Nos. in Fig. 2	Name of compound	Color of solution in ethanol in the presence of sodium alcoholate	Absorption bands maxima		
			$\epsilon \cdot 10^{-2}$	log ϵ	λ mμ
1	Triphenylamine	Colorless	199.5	3.30	297
2	4-Nitrotriphenylamine	Reddish orange	199.5 230.0	4.30 4.38	420 272
3	4,4'-Dinitrotriphenylamine	Light brown	398.0	4.60	340
4	4,4',4"-Trinitrotriphenylamine	Reddish brown	602.6 602.6	4.78 4.78	400 268

Triphenylamine does not change in the presence of sodium alcoholate, for which reason its spectral curve remains the same as in ethanol solution. An entirely different situation exists for the p-nitro derivatives of triphenylamine. In Fig. 2 we see the sharp difference between the absorption spectra curves of these nitro derivatives and that of triphenylamine itself.

It should be mentioned here that all of the nitro derivatives of triphenylamine show a yellow color in ethanol solution, but with different shades of yellow, while in the presence of sodium alcoholate the solutions of these same substances show a considerably deeper color (Table 2).

Under the influence of 2 moles of sodium alcoholate, the nitro derivatives of triphenylamine acquire a deeper color due to the formation of quinoid structures in the molecules with internal compensation of the positive and negative charges in accord with the scheme:



The other p-nitro derivatives of triphenylamine show a similar structure.

When a comparison is made of the spectrographic data obtained (Tables 1 and 2) for the absorption band maxima in ethanol solution and in ethanol solution in the presence of 2 moles of alcoholate, it can be seen to what extent sodium alcoholate influences the character of the absorption spectra of the studied substances, and consequently their electron structure, and how the solution color changes.

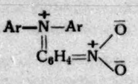
As can be seen from Tables 1 and 2, triphenylamine itself does not show any changes in the maximum of its absorption bands. For 4-nitrotriphenylamine the curve already shows considerable change in its absorption bands. Here one band with its absorption maximum in the extreme ultraviolet (at 254 mμ) disappears. The extreme band for the ethanol solution with an absorption maximum at 397 mμ is shifted toward the long wavelength region by 23 mμ and increases in absorption intensity by 10.9 times, while the band with an absorption maximum at 272 mμ, when compared with the similar band in ethanol solution, is shifted toward the short wavelength region by 10 mμ, while its absorption intensity increases 3.09 times. In this connection the color of the solution changes from yellow to reddish orange.

For 4,4'-dinitrotriphenylamine the change in the absorption spectra curve is even greater. Here a considerable shift toward the long wavelength region from 235 to 340 mμ for the ethanol solution is observed for the maximum of the absorption bands in the extreme ultraviolet, and also the absorption intensity of the given maximum shows a 2.57-fold increase. The second band with an absorption maximum is absent in Fig. 2, evidently for the reason that it must have been greatly shifted toward the visible region. Here the solution color changes from yellow to light brown.

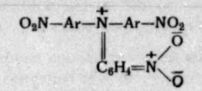
The curve for the absorption spectra of 4,4',4"-trinitrotriphenylamine showed but slight change in the wavelengths when compared with the ethanol solution. Thus, the maximum of the absorption bands in the short wavelength region was shifted toward the long wavelengths by 16 mμ, but at the same time the absorption intensity increased 6.6 times. On the other hand, the maximum of the second band (at 405 mμ) was shifted by 5 mμ toward the short wavelength region, while the maximum absorption intensity again showed considerable rise and increased 2.5 times. In its bands with absorption maxima this curve copies, as it were, the 4-nitrotriphenylamine curve due to the similarity in the electron structures of these molecules.

Here the solution color for the trinitrotriphenylamine changes from yellow to reddish brown.

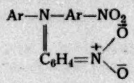
As a result, an interesting rule is established for nitro derivatives of triphenylamine. When either one or three nitro groups are present in triphenylamine, the formation of the quinoid structure is accompanied by the appearance of symmetry in molecules (I) and (II),



$\mathrm{Ar{-}\overset{+}{N}(Ar){=}C_6H_4{=}\overset{+}{N}(\bar{O})\bar{O}}$ (I)



$\mathrm{O_2N{-}Ar{-}\overset{+}{N}(Ar{-}NO_2){-}C_6H_4{=}\overset{+}{N}(\bar{O})\bar{O}}$ (II)



$\mathrm{Ar{-}N(Ar{-}NO_2){-}C_6H_4{=}\overset{+}{N}(\bar{O})\bar{O}}$ (III)

and consequently their absorption spectra curves are similar, whereas for the dinitrotriphenylamine under the same conditions there occurs complete asymmetry of (III), which explains the sharp change in the character of the absorption spectra curve of this compound.

SUMMARY

1. The considerable influence exerted by a fractional nitro group on the character of absorption spectra when compared with the curve for triphenylamine is clearly manifested in ethanol solution.

2. Considerable change in the character of the absorption spectra for p-nitro derivatives of triphenylamine occurs under the influence of sodium alcoholate. The change in the color of substances in alcoholate solution is associated with a change in substance structure, i.e. with the formation of a quinoid type of molecule.

3. A considerable influence on the character of the absorption spectra curves is shown by the symmetrical and asymmetrical position of the molecules in nitro derivatives of triphenylamine.

LITERATURE CITED

[1] P. M. Bugai, J. Gen. Chem. 23, 605 (1953) (T.p. 627).*

[2] W. A. Schroeder, P. E. Wilcox, K. N. Trueblood and A. O. Dekker, Anal. Chem. 23, 1740 (1951).

[3] Baker, J. Chem. Soc. 91, 1496 (1907).

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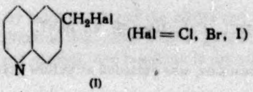
PREPARATION OF 6-MONOHALOMETHYLQUINOLINES

B. P. Lugovkin

Due to the availability at the present time of primary quinolylcarbinols, especially of 6-quinolylcarbinol [1], it seemed of interest to prepare and study the chemical properties of 6-halomethylquinolines (I):



(I)

There is some data in the literature on the preparation of 2,4,8-monohalomethylquinolines [2], synthesized from either di- and tribromo- or trichloromethyl derivatives of quinoline under heating with hydrogen halide acids. 3-Bromomethylquinoline was synthesized by the reaction of phosphorus tribromide with 3-quinolylcarbinol [3]. Of the iodo derivatives the 8-iodomethylquinoline was obtained by heating 8-bromomethylquinoline with methyl iodide [4], without forming its methiodide.

We prepared the 6-chloro- and 6-bromomethylquinolines in respective yields of 81 and 55% by heating 6-quinolylcarbinol and its hydrohalides with the corresponding concentrated hydrogen halide acids [5].

The 6-bromomethylquinoline is the less stable compound, showing change when heated, during recrystallization, and when stored for a short time. The 6-chloro- and 6-bromomethylquinolines were characterized as the picrates and as the hydrogen halide salts.

An attempt to synthesize the 6-iodomethylquinoline by the reaction of anhydrous sodium iodide with the chloromethylquinoline in acetone solution proved unsuccessful, although we did isolate the hydriodide in 21% yield. Reaction of the latter with picric acid in alcohol solution gave the 6-iodomethylquinoline picrate. Repetition of the experiment in methanol solution did not yield any iodo derivatives of 6-methylquinoline.

6-Chloromethylquinoline did not react with metallic magnesium when heated in either benzene or ether solution. The same chloride readily reacted with sodium ethylate and methylate to give the corresponding 6-quinolylcarbinol ethers, which were oily liquids. The ethers were identified as the methiodides.

The heating of the chloride with potassium cyanide in alcohol solution gave 6-quinolylacetonitrile in 23% yield. The reaction was accompanied by the formation of a tarry product. The methiodide of the nitrile was prepared.

EXPERIMENTAL

6-Quinolylcarbinol was obtained by the Rodionov-Berkenheim method [1] and was recrystallized from a mixture of light benzine and dioxane, m.p. 79-81°.

The hydrochloride of the carbinol was obtained by its treatment with dilute hydrochloric acid (1:1) and subsequent evaporation. Tiny colorless needles with m.p. 204-205° (from ethanol). Readily soluble in water and more difficultly soluble in alcohol.

Found %: Cl 18.06.* $C_{10}H_{10}ONCl$. Calculated %: Cl 18.13.

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*The halogens were determined by the Carius method.

The hydrobromide was prepared by passing hydrogen bromide into a solution of the carbinol in anhydrous ethanol. Colorless needles with m.p. 201° (from ethanol). Readily soluble in water and more difficultly soluble in alcohol.

Found %: Br 33.94. $C_{10}H_{10}ONBr$. Calculated %: Br 33.30.

The treatment of either the hydrochloride or hydrobromide with picric acid gave the 6-quinolylcarbinol picrate, m.p. 201°.

Preparation of 6-chloromethylquinoline. A mixture of 6 g of the carbinol and 34 ml of hydrochloric acid (d 1.19) was heated in a sealed tube at 135-140° for 7 hours. The solution was neutralized with soda, the separated precipitate was washed with water and the next day was extracted (in an extractor) with light benzine. Here 5.4 g (80.6%) of 6-chloromethylquinoline was obtained as light yellow crystals with m.p. 68-70°. Its mixture with the carbinol melted at 53-58°. On heating the mixture with activated charcoal in ether solution, colorless crystals with m.p. 70° were obtained (the melting point did not change under repeated heating).

This chloride shows lachrymatory properties. Readily soluble in ether, alcohol and benzene, more difficultly soluble in light benzine and cyclohexane, and difficultly soluble in water.

Found %: Cl 20.19, 19.63. $C_{10}H_8NCl$. Calculated %: Cl 19.97.

The picrate, prepared in alcohol solution, was obtained as yellow crystals with m.p. 206° (from glacial acetic acid).

Found %: Cl 8.67. $C_{10}H_8NCl \cdot C_6H_3O_7N_3$. Calculated %: Cl 8.72.

6-Chloromethylquinoline Hydrochloride was obtained by passing hydrogen chloride into a solution of the compound in anhydrous ethanol. Crystals with m.p. 181-182° (from anhydrous ethanol). Readily soluble in water and more difficultly soluble in alcohol.

Found %: Cl 32.96. $C_{10}H_9NCl_2$. Calculated %: Cl 33.14.

Treatment of the hydrochloride with picric acid in ethanol solution gave the 6-chloromethylquinoline picrate with m.p. 206° (mixed melting point).

Reaction with sodium methylate and ethylate. 1) 6-Quinolylcarbinol methyl ether. To 3 g of the chloride in 15 ml of anhydrous methanol was added an alcohol solution of sodium methylate (0.4 g of sodium in 10 ml of anhydrous methanol). Sodium chloride separated when the mixture was heated on the water bath at 75-80° for 10 minutes. After dilution with water the product was extracted with chloroform. The heating with activated charcoal in acetone gave 1.7 g of 6-quinolylcarbinol methyl ether as a rose colored oily liquid, which became very thick when heated at 140 to 180°. The picrate was obtained as dark yellow crystals with m.p. 175-176° (from ethanol), and the chloroaurate as light yellow crystals with m.p. 183° (from glacial acetic acid).

The methiodide was obtained from 0.7 g of the ether and 1.5 ml of methyl iodide by heating on the water bath at 75-80° for 15 minutes. The yield of the methiodide was 0.95 g (74.8%). After heating in anhydrous ethanol with activated charcoal the compound was obtained as yellow crystals with m.p. 138-139°. Readily soluble in water and alcohol, and insoluble in dry ethyl ether.

Found %: I 39.74, 40.07. $C_{12}H_{14}ONI$. Calculated %: I 40.29.

2) 6-Quinolylcarbinol ethyl ether. The synthesis was run under the conditions of the experiment with sodium methylate. From 3.5 g of the chloride and 0.5 g of metallic sodium we obtained 2.9 g of 6-quinolylcarbinol ethyl ether as a colorless liquid (after heating with activated charcoal in diethyl ether). The picrate was obtained as yellow crystals with m.p. 175-176° (from ethanol). The chloroaurate was obtained as golden yellow crystals with m.p. 175° (from glacial acetic acid).

The methiodide was obtained from 0.75 g of the ether and 1.5 ml of methyl iodide in a yield of 1.2 g (91%). After recrystallization from a mixture of dioxane and anhydrous ethanol it was obtained as yellow crystals with m.p. 118-119°. Readily soluble in water and alcohol, very difficultly soluble in dioxane, and insoluble in dry ether.

Found %: I 38.65, 38.94. $C_{13}H_{16}ONI$. Calculated %: I 38.57.

Reaction with potassium cyanide. A mixture of 13.6 g of 6-chloromethylquinoline in 50 ml of ethanol and 5.1 g of potassium cyanide in 5 ml of water was heated on the water bath at 80° for 1 hour. The reaction mixture was diluted with water, and after salting out with sodium chloride, the reaction product was extracted with ether. The yield of 6-quinolylacetonitrile was 3 g (23.3%). On being heated twice with activated charcoal in acetone it was obtained as colorless crystals with m.p. 81°; after recrystallization from water, m.p. 81.5°. The substance is readily soluble in acetone, alcohol and ether and, when heated, in benzene and water.

Found %: N 16.23 (Kjeldahl). $C_{11}H_8N_2$. Calculated %: N 16.67.

The picrate of the nitrile, prepared in alcohol solution, was obtained as dark yellow crystals with m.p. 217.5° (from glacial acetic acid).

The methiodide was obtained by heating 0.3 g of the nitrile and 1 ml of methyl iodide on the boiling water bath for 30 minutes. Recrystallization from ethyl alcohol gave 0.45 g of dark yellow crystals with m.p. 167-168°. Readily soluble in water and alcohol, and insoluble in dry ether.

Found %: I 41.20, 40.70. $C_{12}H_{11}N_2I$. Calculated %: I 40.94.

Preparation of 6-bromomethylquinoline. Hydrogen bromide was passed through a mixture of 4.6 g of the carbinol and 25 ml of water until saturated. The mixture was heated in a sealed tube at 120-130° for 7 hours. The next day the crystalline precipitate was separated (6-bromomethylquinoline hydrobromide). After suitable treatment 3.5 g (54.5%) of 6-bromomethylquinoline with m.p. 71° was obtained. Recrystallization from light benzine gave 2 g of colorless crystals with m.p. 74-75°.

The bromide shows lachrymatory properties. Readily soluble in ether and alcohol, and, when heated in light benzine and cyclohexane, difficultly soluble in water.

Found %: Br 35.34, 35.86. $C_{10}H_8NBr$. Calculated %: Br 36.00.

When stored for a month the bromine content of the bromide dropped to 29.65%. The substance does not melt below 230°.

The picrate, prepared in alcohol solution, was obtained as yellow crystals with m.p. 198° (from glacial acetic acid).

Found %: Br 17.39. $C_{10}H_8NBr \cdot C_6H_3O_7N_3$. Calculated %: Br 17.72.

The hydrobromide, isolated in one of the experiments, was obtained as tiny needles with m.p. 201° (from ethanol). Readily soluble in water and more difficultly soluble in alcohol.

Found %: Br 52.84. $C_{10}H_9NBr_2$. Calculated %: Br 52.77.

Treatment of the hydrobromide with picric acid in ethanol solution gave the 6-bromomethylquinoline picrate, m.p. 198° (mixed melting point).

Preparation of 6-iodomethylquinoline. To 2.5 g of 6-chloromethylquinoline in 10 ml of anhydrous acetone was added 2.5 g of anhydrous sodium iodide in 20 ml of acetone. Periodic shaking for 1.5 hours gave a yellow precipitate, which proved to be completely soluble in water. The product was salted out with sodium chloride, dried, and extracted first with dry ether, and then with methanol. Only a small amount of residue was obtained from the ether solution, while the methanol solution gave 1.2 g (21.5%) of golden yellow crystals with m.p. 203°. Recrystallization from ethanol gave dark orange crystals with m.p. 204-205°. Readily soluble in water and when heated – in ethyl alcohol, more difficultly in methyl alcohol, and insoluble in dry ether.

Found %: I 64.19. $C_{10}H_8NI \cdot HI$. Calculated %: I 63.95.

Treatment of the hydriodide with picric acid in ethanol solution gave the 6-iodomethylquinoline picrate as yellow green crystals with m.p. 198° (from ethanol).

Found %: I 25.27. $C_{10}H_8NI \cdot C_6H_3O_7N_3$. Calculated %: I 25.49.

SUMMARY

1. The heating of 6-quinolylcarbinol with hydrogen halide acids gave the 6-chloro- and 6-bromomethylquinolines.

2. A number of reactions was run with the 6-chloromethylquinoline, and in one of them, the reaction with anhydrous sodium iodide in anhydrous acetone solution gave the 6-iodomethylquinoline hydriodide.

LITERATURE CITED

[1] V. M. Rodionov and M. A. Berkenheim, J. Gen. Chem. 14, 501, 1126 (1944); B. P. Lugovkin, J. Gen. Chem. 23, 1696 (1953) (T.p. 1785).*

[2] J. Howitz and P. Nother, Ber. 39, 2708 (1906); D. L. Hammick, J. Chem. Soc. 1926, 1302; K. N. Campbell, J. Ackerman and B. Campbell, J. Am. Chem. Soc. 71, 2905 (1949); B. R. Brown, D. L. Hammick and B. H. Thewlis,, J. Chem. Soc. 1951, 1145, M.M. Hasegawa, C. A. 46, 511 (1952).

[3] B. R. Brown, D. L. Hammick and B. H. Thewlis, J. Chem. Soc. 1951, 1146.

[4] J. Höwitz, Ber. 35, 1273 (1902).

[5] K. Löffer, Ber. 37, 164 (1904).

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Central Council of Trade Unions

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*T.p. = C. B. Translation pagination.

THE SYNTHESIS OF AROMATIC ISOCYANATES

D. F. Kutepov and N. S. Rozanova

Both aromatic and aliphatic isocyanates are easily obtained by heating the corresponding carbamoyl chlorides, usually in an inert solvent, at their dehydrochlorination temperatures [1].

We obtained the 2,4,5- and 3,4,5-trichlorophenyl isocyanates by heating in dichloroethane the 2,4,5- and 3,4,5-trichlorophenylcarbamoyl chlorides, in turn obtained from the corresponding anilines and phosgene. In both cases small amounts of hexachlorodiphenylureas were obtained in the reaction.

The heating of 2,4,5-trichlorophenylcarbamoyl chloride in ethyl acetate solution results in exchange reaction with the formation of ethyl trichlorophenylcarbamate in accord with the equation:

$$C_6H_2Cl_3NHCOCl + C_2H_5O_2CCH_3 \rightarrow C_6H_2Cl_3NHCO_2C_2H_5 + CH_3COCl.$$

The structure of the obtained ester was established by its analysis, and also by the fact that the melting point was not depressed when this compound was mixed with authentic ethyl 2,4,5-trichlorophenylcarbamate.

A number of mothproofing agents are described in a series of Swiss patents [2], which are condensation products of aromatic isocyanates with complex aromatic amines, as for example, with 2-amino-4,4'-dichloro-1,1'-diphenyl ether-2'-sulfonic acid, 2-amino-4'-chloro-1,1'-diphenyl ether-2'-sulfonic acid, etc.

To obtain these substances either 2,4,5- or 3,4,5-trichloroaniline is reacted with phosgene in ethyl acetate medium until the corresponding carbamoyl chloride is formed; then the solvent is distilled off under heating, in which connection the carbamoyl chloride loses hydrogen chloride and is transformed into the isocyanate, which is then reacted with the desired amine.

When the preparation of the 2,4,5- and 3,4,5-trichlorophenyl isocyanates was attempted by the method and under the conditions given in the above patents, we found that in addition to the main reaction leading to the formation of isocyanates, there were other reactions, since together with the isocyanate a hexachlorodiphenylurea was also formed. Here we were able to isolate the trichlorophenyl isocyanate only in small yield, in which connection the reaction product contained 50% and more of the hexachlorodiphenylurea. However, if the solvent (ethyl acetate) is vacuum-distilled from the reaction mixture at a temperature not exceeding 30°, then the trichlorophenyl isocyanate yield reaches 75%.

It is evident that the formation of large amounts of hexachlorodiphenylurea in the decomposition of the carbamoyl chloride by direct heating of the reaction mixture is associated with the presence of a large amount of hydrogen chloride in this mixture. At elevated temperature the hydrogen chloride decomposes the formed ethyl trichlorophenylcarbamate with the formation of trichloroaniline, which then reacts with the carbamoyl chloride, yielding the urea. It is known that such decomposition of carbamic acid esters under the influence of hydrogen chloride proceeds in acetic acid, dioxane and anhydrous ethyl alcohol medium [3]. However, when we treated a hot solution of ethyl 2,4,5-trichlorophenylcarbamate in ethyl acetate with hydrogen chloride, we established that the ester fails to show change under these conditions. It is possible that the hydrogen chloride reacts with the carbamoyl chloride to give trichloroaniline and phosgene, the reaction of which with each other leads to the hexachlorodiphenylurea by the scheme

$$C_6H_2Cl_3NHCOCl + HCl \rightarrow C_6H_2Cl_3NH_2 + COCl_2,$$

$$2C_6H_2Cl_3NH_2 + COCl_2 \rightarrow (C_6H_2Cl_3NH)_2CO + 2HCl.$$

That the last reactions are possible is supported by the decomposition of the pure trichlorophenylcarbamoyl chloride to the isocyanate when it is heated in ethyl acetate medium in the presence of hydrogen chloride. Here we were able to isolate both the hexachlorodiphenylurea and the trichloroaniline.

Besides the ethyl ester of 2,4,5-trichlorophenylcarbamic acid, we also prepared the methyl and n-propyl esters from 2,4,5-trichloroaniline and the corresponding chloroformates, while from 2,4,5-trichlorophenylcarbamoyl chloride and ethylene chlorohydrin we obtained the β-chloroethyl ester of the same acid.

EXPERIMENTAL

2,4,5-Trichlorophenylcarbamoyl chloride from 2,4,5-trichloroaniline and phosgene. To 35 g of phosgene dissolved in 38 g of dry ethyl acetate at 0 to 5°, and with stirring, was gradually added a solution of 15 g of 2,4,5-trichloroaniline in 83 g of ethyl acetate.

After 20 minutes at 0 to 5° the temperature of the reaction mixture was raised to 20° and kept here for 30-50 minutes. Then a stream of gaseous phosgene was passed through the reaction mixture. The obtained 2,4,5-trichlorophenylcarbamoyl chloride was filtered and washed with ethyl acetate. Yield 74.6% (based on the trichloroaniline).

Found %: C 32.31, 31.92; H 1.63, 1.48; N 5.51, 5.48; Cl 54.46, 54.71. $C_7H_3ONCl_4$. Calculated %: C 32.43; H 1.14; N 5.4; Cl 54.82.

The preparation of 3,4,5-trichlorophenylcarbamoyl chloride was run at a temperature of 0 to –4° from beginning to end, in which connection the formed 3,4,5-trichlorophenylcarbamoyl chloride went into solution. To isolate the trichlorophenylcarbamoyl chloride, the ethyl acetate was evaporated in vacuo at a temperature not exceeding 10°.

2,4,5-Trichlorophenyl isocyanate from 2,4,5-trichlorophenylcarbamoyl chloride. A solution of 2,4,5-trichlorophenylcarbamoyl chloride in dry dichloroethane was heated on the water bath for 2.5 hours. The precipitate obtained during reaction was filtered and found to have m.p. 304°, which corresponds to the m.p. of the 2,2',4,4',5,5'-hexachlorodiphenylurea obtained by us from 2,4,5-trichloroaniline and phosgene. Evaporation of the filtrate at room temperature gave white crystals of 2,4,5-trichlorophenyl isocyanate with m.p. 61°.

Found %: C 37.49, 37.42; H 1.26, 1.08; N 6.59, 6.69. $C_7H_2ONCl_3$. Calculated %: C 37.75; H 0.89; N 6.25.

3,4,5-Trichlorophenyl isocyanate with m.p. 53.5° was obtained in a similar manner from 3,4,5-trichlorophenylcarbamoyl chloride.

Ethyl 2,4,5-trichlorophenylcarbamate.

a) From 2,4,5-trichlorophenylcarbamoyl chloride and ethyl acetate. A mixture of 15 g of 2,4,5-trichlorophenylcarbamoyl chloride and 100 ml of dry, alcohol-free ethyl acetate was placed in a Wurtz flask. The ethyl acetate, which was collected in a receiver containing 50 ml of ice water, was distilled from the mixture by heating on the water bath.

The solid residue obtained after distilling off the ethyl acetate (11.46 g), was treated with hot carbon tetrachloride, where 3.06 g of 2,2',4,4',5,5'-hexachlorodiphenylurea with m.p. 308° remained undissolved. The substance isolated from the carbon tetrachloride, after recrystallization from the same solvent, melted at 92°. Its mixed melting point with authentic ethyl 2,4,5-trichlorophenylcarbamate (see below) was not depressed.

Found %: C 39.89, 40.00; H 3.31, 3.42; N 5.41, 5.54. $C_9H_8O_2NCl_3$. Calculated %: C 40.22; H 2.97; N 5.21.

The water layer, obtained in the receiver, was qualitatively shown to contain acetic acid (indigo color with benzaldehyde).

Ethyl 3,4,5-trichlorophenylcarbamate with m.p. 132.5° was obtained in a similar manner.

b) From 2,4,5-trichloroaniline and ethyl chloroformate. A mixture of 2,4,5-trichloroaniline with excess ethyl chloroformate was heated on the water bath for 3 hours. The excess ethyl chloroformate was distilled, while the obtained solid residue was recrystallized from chloroform. The ethyl 2,4,5-trichlorophenylcarbamate melted at 91°. The methyl and n-propyl 2,4,5-trichlorophenylcarbamates were obtained in a similar manner, melting respectively at 103 and 70°.

c) From 2,4,5-trichlorophenylcarbamoyl chloride and ethyl alcohol. A mixture of 10 g of 2,4,5-trichlorophenylcarbamoyl chloride and 70 g of ethyl alcohol was heated on the boiling water bath for 3 hours. The obtained ethyl 2,4,5-trichlorophenylcarbamate melted at 91-92°.

β-Chloroethyl 2,4,5-trichlorophenylcarbamate. A mixture of 17 g of 2,4,5-trichlorophenylcarbamoyl chloride and 60 ml of dry ethylene chlorohydrin was heated for 3 hours at 129°. The mixture on cooling deposited white crystals of β-chloroethyl 2,4,5-trichlorophenylcarbamate, which after recrystallization from chloroform melted at 98-100°.

Found %: C 36.4, 36.13; H 3.24, 3.18; N 5.13, 4.93. $C_9H_7O_2NCl_4$. Calculated %: C 35.64; H 2.31; N 4.62.

Preparation of 2,4,5-trichlorophenyl isocyanate from 2,4,5-trichloroaniline and phosgene.

a) As indicated above, the reaction of 32 g of phosgene with 10 g of 2,4,5-trichloroaniline gave the trichlorophenylcarbamoyl chloride.

On conclusion of reaction the ethyl acetate was distilled off under heating. The residue was extracted with chloroform. Not more than 50% of the residue went into solution here. The substance isolated from the chloroform had m.p. 55-61° (the 2,4,5-trichlorophenyl isocyanate obtained in the dehydrochlorination of 2,4,5-trichlorophenylcarbamoyl chloride by heating it in dichloroethane has m.p. 61°). The chloroform-insoluble portion of the residue melted at 303° (the m.p. of 2,2',4,4',5,5'-hexachlorodiphenylurea is 303-306°).

When the experiment was run with 3,4,5-trichloroaniline, the residue, after distilling off the ethyl acetate, consisted entirely of 3,3',4,4',5,5'-hexachlorodiphenylurea (m.p. > 300°; m.p. of 3,4,5-trichlorophenyl isocyanate 53.5°).

b) The reaction mixture, containing 2,4,5-trichlorophenylcarbamoyl chloride (prepared by the above-described method from 10 g of 2,4,5-trichloroaniline), was diluted with ethyl acetate (200 ml) and kept at 20° in the vacuum of a water-jet pump to remove any phosgene and hydrogen chloride. The ethyl acetate also distilled with the gases. Toward the end of distillation the temperature of the mixture was gradually raised to 30°. The residue was treated with chloroform, from which 8.4 g (74.24%, based on charged trichloroaniline) of 2,4,5-trichlorophenyl isocyanate with m.p. 60-61° was isolated. The amount of hexachlorodiphenylurea obtained here did not exceed 1.46 g (m.p. 303°).

Reaction of 2,4,5-trichlorophenylcarbamoyl chloride with hydrogen chloride. A mixture of 3 g of 2,4,5-trichlorophenylcarbamoyl chloride and 75 ml of ethyl acetate, saturated with 15 g of hydrogen chloride, was heated for 50 minutes on the water bath, at the same time passing a stream of dry hydrogen chloride through the mixture. Then the mixture was cooled; the obtained white glistening crystals (1.15 g) were filtered; they melted with decomposition at 170-179° and contained 15.52% chlorine, which was cleaved when the substance was treated with water (the hydrochloride of 2,4,5-trichloroaniline contains 15.23% of labile chlorine). The substance treated with water had m.p. 95-96.5°, which corresponds to the melting point of 2,4,5-trichloroaniline. The solid residue (1.73 g) obtained from the evaporation of the mother liquor also contained a large amount of labile chlorine and 0.14 g of 2,2',4,4',5,5'-hexachlorodiphenylurea with m.p. 300°.

SUMMARY

1. The heating of 2,4,5-trichlorophenylcarbamoyl chloride with ethyl acetate devoid of hydrogen chloride results in exchange reaction with the formation of ethyl 2,4,5-trichlorophenylcarbamate.

2. In the preparation of the 2,4,5- and 3,4,5-trichlorophenyl isocyanates from the corresponding trichloroanilines and phosgene via the preparation of the trichlorophenylcarbamoyl chloride and its subsequent dehydrochlorination by direct heating of the reaction mixture there proceeds, in addition to the main reaction,

the reaction of forming the hexachlorodiphenylurea, conditioned by the presence of a large amount of hydrogen chloride in the reaction mixture.

3. The methyl and n-propyl esters of 2,4,5-trichlorophenylcarbamic acid were prepared by reacting 2,4,5-trichloroaniline with the corresponding chloroformates, and the β-chloroethyl ester of the same acid was obtained from 2,4,5-trichlorophenylcarbamoyl chloride and ethylene chlorohydrin.

LITERATURE CITED

[1] A. A. Blagonravova and G. A. Levkovich, Progr. Chem. 24, 93 (1955); U.S. Patent 2480088; C.A. 44, 1136 (1950); German Patent 801993; C.A. 45, 5178 (1951); German Patent 133760- Chem. Zentr. 1902, II, 553; L. F. Fieser and H. J. Creech, J. Am. Chem. Soc. 61, 3502 (1939); British Patent 483308; C.A. 32, 7056 (1938); German Patent 224490; Frdl. 10, 658; H. Fraenkel-Conrat and H. S. Olcott, J. Am. Chem. Soc. 66, 845 (1944).

[2] Swiss Patents 215291-215329; C.A. 42, 6853 (1948); Chem. Zentr. 1942, I, 2479.

[3] D. Ben-Ishai and A. Berger, J. Org. Chem. 17, 1564 (1952).

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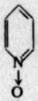
HETEROCYCLIC N-OXIDES

III. POLAROGRAPHIC REDUCTION OF SOME HETEROCYLIC N-OXIDES

L. V. Varyukhina and Z. V. Pushkareva

The N-oxides of nitrogen-containing heterocyclic compounds deserve considerable interest and have been intensely studied in recent years, especially with respect to the N-oxides of pyridine and quinoline [1].

In previous communications we described the synthesis and chemical properties of N-oxides of the acridine series [2], and also the results of measuring the dipole moments of a number of heterocyclic N-oxides, where the change in properties in going from the N-oxide of the simplest heterocycle – pyridine (I) – to the N-oxides and N,N-dioxides of heterocycles with condensed systems (I)-(VII) could be followed: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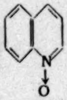
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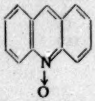
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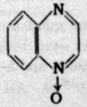
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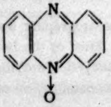
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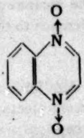
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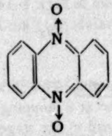
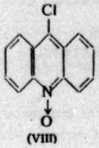

(VII)

From the results of measuring the dipole moments it was established that for phenylene rings condensed with pyridine there exists a mutual influence between the oxide oxygen and the electron systems of these rings, expressed in a reduction of the polarity of the N → O bond. The same rule is also observed when there is an accumulation of phenylene rings in the pyrazine system.

In recent years the polarographic reduction method [3-5] has become the method most frequently used to characterize the properties of organic substances. In particular, the problem of the ease of reduction of N-oxides of the pyridine and quinoline series at a dropping-mercury electrode has begun to be examined.

We used this method to study the heterocyclic N-oxides in order to characterize quantitatively the reduction capacity shown by the $N \rightarrow O$ bond as a function of the chemical structure of the molecule and attempt to uncover the same rule for the mutual influence of the semipolar $N \rightarrow O$ with the whole heterocyclic system. In addition to the above indicated series of N-oxides (I)-(VII) we also studied the N-oxides of the acridine series (VIII)-(XI), the N-oxide of dimethylaniline (XII) and several unoxidized heterocyclic bases.

The substances from (I) through (VIII) were synthesized by methods described in the literature, while the synthesis of substances (IX), (X) and (XI) was described in the previous communication [2]. All of the substances were thoroughly purified by recrystallization to constant melting point.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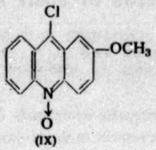
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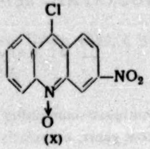
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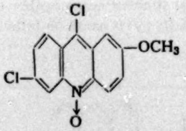
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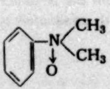
(XII)

A Geirovsky micropolarograph was used for the polarographic studies, with which the curves showing the relationship between the amperage and the voltage were automatically obtained and photographically recorded.

Depending on the height of the polarographic waves the measurements were made with a galvanometer sensitivity ranging from 1/10 to 1/50. Most of the N-oxides were studied at a concentration of $1 \cdot 10^{-3}$ M. Exceptions were the N-oxides of 2-methoxy-6,9-dichloroacridine and 3-nitro-9-chloroacridine, which, due to their low solubility, were polarographed at a concentration of $1 \cdot 10^{-4}$ M. All of the measurements were run in alcohol solution with acetate buffer.

The polarographic curves are shown in Figs. 1-14. The measurement results are summarized in Table 1. All of the values of the half-wave potentials ($E_{1/2}$) are in reference to the potential of a saturated calomel electrode (s.c.e).

Discussion of the measurement results. The obtained data serve as evidence that heterocyclic N-oxides are capable of being irreversibly reduced at a dropping-mercury electrode. In this connection all of the unsubstituted heterocyclic N-oxides are reduced in one stage. Exceptions are the phenazine mono- and dioxides, which give two polarographic waves corresponding to the reduction of the oxide oxygen and of the heterocycle itself.

As regards the N-oxides of the 9-chloroacridine derivatives, then, in contrast to acridine N-oxide, they give two polarographic waves. A comparison of the polarograms of these N-oxides with those of the corresponding unoxidized heterocycles shows that the appearance of the second ill-defined wave is not associated with the introduction of oxide oxygen, but instead is conditioned by the chemical properties of the unoxidized heterocycle itself.

The reduction of 3-nitro-9-chloroacridine N-oxide proceeds in three steps, in which connection the first corresponds to the reduction of the nitro group.

TABLE 1

Name of substance	Concentration (M)	Half-wave potential in volts (relative to s.c.e)	Limiting diffusion current (ma)
Pyridine N-oxide (I)	$1 \cdot 10^{-3}$	−1.364	2.70
Quinoline N-oxide (II)	$1 \cdot 10^{-3}$	−1.164	6.47
Acridine N-oxide (III)	$1 \cdot 10^{-3}$	−0.854	4.66
Quinoxaline monoxide (IV)	$1 \cdot 10^{-3}$	−0.650	9.10
Phenazine monoxide (V)	$1 \cdot 10^{-3}$	−0.218, −0.382	3.50, 3.10
Quinoxaline dioxide (VI)	$1 \cdot 10^{-3}$	−0.618	10.36
Phenazine dioxide (VII)	$1 \cdot 10^{-3}$	−0.218, −0.364	7.77, 4.04
9-Chloroacridine N-oxide (VIII)	$1 \cdot 10^{-3}$	−0.746, −1.508	7.77, 1.03
9-Chloroacridine (VIIIa)	$1 \cdot 10^{-3}$	−0.636, −1.490	4.66, 1.81
2-Methoxy-9-chloroacridine N-oxide (IX)	$1 \cdot 10^{-3}$	−0.773, −1.472	7.80, 1.52
3-Nitro-9-chloroacridine N-oxide (X)	$1 \cdot 10^{-4}$	−0.290, −0.854, −1.368	1.09, 0.83, 0.42
3-Nitro-9-chloroacridine (Xa)	$1 \cdot 10^{-4}$	−0.317, −0.680, −1.400	0.94, 1.04, 0.26
2-Methoxy-6, 9-dichloroacridine N-oxide (XI)	$1 \cdot 10^{-4}$	−0.663, −1.290	1.25, 0.31
Dimethylaniline N-oxide (XII)	$1 \cdot 10^{-3}$	−1.018	3.37

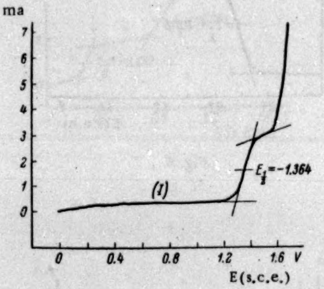

Fig. 1

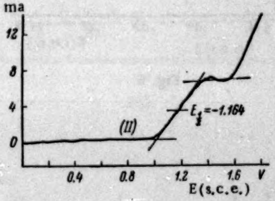

Fig. 2

A comparison of the half-wave potentials of the studied heterocyclic N-oxides permits establishing the following.

1. In the transition from the N-oxide of pyridine to the N-oxides of quinoline and acridine, and also from the mono-and dioxides of quinoxaline to the corresponding oxides of phenazine, the half-wave potentials are shifted toward more positive values. In other words, the accumulation of condensed phenylene rings facilitates reduction of the semipolar N → O bond.

2. In the transition from the N-oxides of quinoline and acridine to the monoxides of quinoxaline and phenazine there is also a corresponding shift in the half-wave potentials toward more positive values, i.e. the introduction of a second unoxidized heteroatom into the molecule of the heterocyclic N-oxide facilitates reduction of the semipolar N → O bond.

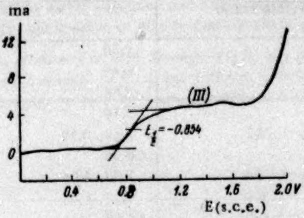

Fig. 3

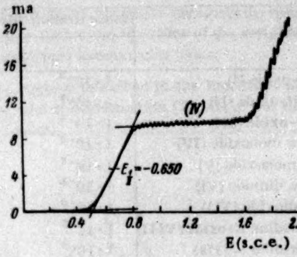

Fig. 4

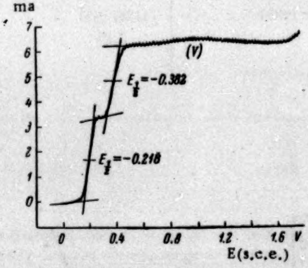

Fig. 5

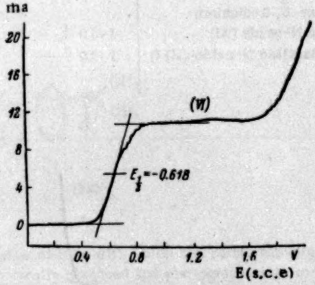

Fig. 6

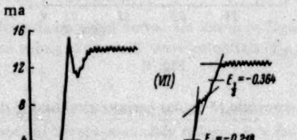

Fig. 7

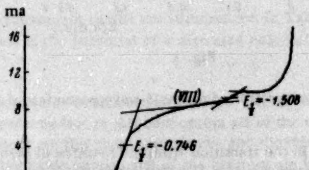

Fig. 8

3. The introduction of certain substituents into the molecule of the acridine N-oxide facilitates to varying degree the reduction of the semipolar N → O bond.

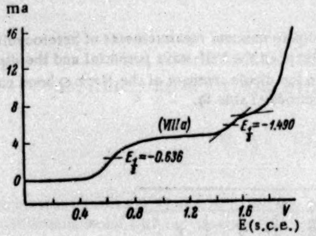

Fig. 9

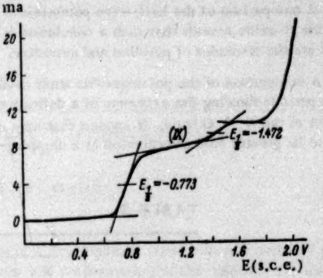

Fig. 10

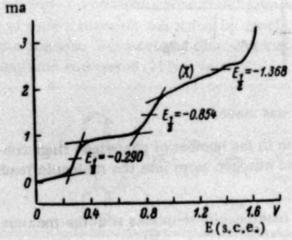

Fig. 11

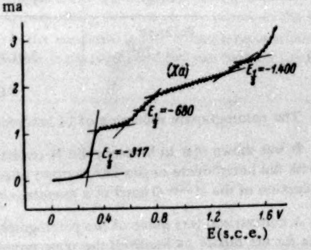

Fig. 12

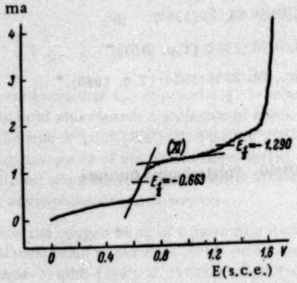

Fig. 13

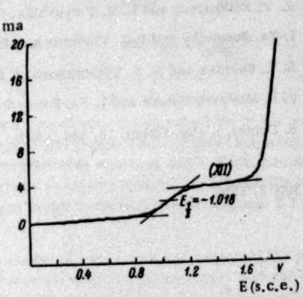

Fig. 14

The conclusion made earlier by Ochiai [6] that the N → O bond in heterocyclic N-oxides is reduced with greater difficulty than in the N-oxides of aliphatic and aliphatoaromatic amines is not supported by the presented data. A comparison of the half-wave potentials of heterocyclic N-oxides with the half-wave potential of dimethylaniline N-oxide reveals that such a conclusion is valid only in the particular case where the heterocyclic N-oxides are the N-oxides of pyridine and quinoline.

A comparison of the polarographic study results with the dipole moment measurements of heterocyclic N-oxides permits showing the existence of a definite relationship between the half-wave potential and the dipole moment of the N → O bond. It appears that here a reduction in the dipole moment of the N → O bond corresponds to its greater ease of reduction at a dropping-mercury electrode (Table 2).

TABLE 2

	N-Oxides				
	pyridine	quinoline	acridine	quin-oxaline	phena-zine
Capacity for reduction ($E_{1/2}$)	−1.36<	−1.16<	−0.854	−0.650<	−0.218
Polarity ($\mu \cdot 10^{18}$)	3.01>	2.80>	2.62	1.86	>1.76

SUMMARY

1. The polarographic reduction of 14 heterocyclic compounds was made.

2. It was shown that in heterocyclic N-oxides either an increase in the number of phenylene rings condensed with the heterocycle or the introduction of a second unoxidized nitrogen atom into the molecule leads to easier reduction of the N → O bond at a dropping-mercury electrode.

3. A comparison was made of the polarographic study data for heterocyclic N-oxides with the measurement data for the dipole moments of the same compounds.

LITERATURE CITED

[1] C. C. J. Culvenor, Revs. Pure and Appl. Chem. (Australia) 3, 83 (1953).

[2] Z. V. Pushkareva and L. V. Varyukhina, Proc. Acad. Sci. USSR 103, 257 (1955).

[3] I. Ya. Postovsky and I. F. Vladimirtsev, Proc. Acad. Sci. USSR 84, 73 (1952).

[4] M. I. Bobrova and N. S. Tikhomirova, J. Gen. Chem. 22, 2098 (1952).(T.p. 2151).*

[5] F. F. Medovshchikova and I. Ya. Postovsky, J. Gen. Chem., 24, 2024 (1954) (T.p. 1989).*

[6] E. Ochiai, J. Org. Chem. 18, 534 (1953).

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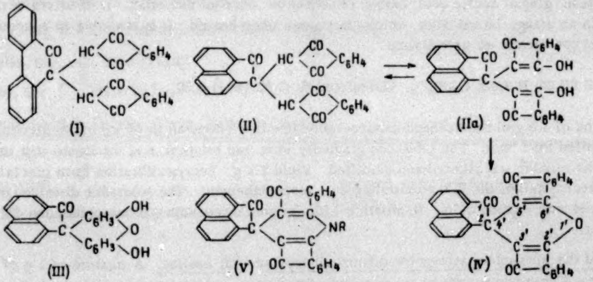
* T.p. = C. B. Translation pagination.

CYCLIZATION OF 2,2-DIINDANDIONYL-1-ACENAPHTHENONE

G. Ya. Vanag and L. S. Geita

In previous studies [1,2] we had shown that two molecules of 1,3-indandione react with one carbonyl group of phenanthrenequinone with the cleavage of a molecule of water and the formation of the colorless 9,9-diindandionyl-10-phenanthrone (I). The reaction proceeds in a similar manner with acenaphthenequinone, where the colorless 2,2-diindandionyl-1-acenaphthenone (II) is formed. The latter proved to be less stable than the 9,9-diindandionyl-10-phenanthrone, and when treated with either bromine or sulfuric acid cleaves one molecule of the indandione [3]. 9,9-Diindandionyl-10-phenanthrone easily cleaves a molecule of water from two of its enolic hydroxyl groups and gives the corresponding spiropyran. It was of interest to determine if the more unstable 2,2-diindandionyl-1-acenaphthenone could also be cyclized to the corresponding spiropyran. In principle the possibility of such a reaction was shown by Zsuffa [3] and Matei [4] in the condensation of acenaphthenequinone with diatomic phenols. For example, during reaction a molecule of water is cleaved from the two hydroxyl groups of resorcinol, and compound (III) is formed.



It was found that 2,2-diindandionyl-1-acenaphthenone when treated with acetic anhydride in the presence of sulfuric acid also cleaves a molecule of water from its enolic hydroxyl groups (IIa) and gives the orange-yellow acenaphthenone-1-spiro-(2:4')-2', 3'(CO),6',5'(CO)-dibenzoylenepyran (IV) with m.p. 360°. Similar to the corresponding spiropyran of the phenanthrene series, it is slightly soluble in organic solvents. It is insoluble in aqueous alkali, but when heated with alcoholic alkali, the pyran oxygen bridge is cleaved and the original 2,2-diindandionyl-1-acenaphthenone is recovered.

Since the oxygen atom of a pyran ring readily reacts with ammonia and amines, we examined the possibility of a similar reaction in our case. With aniline the reaction proceeds smoothly in glacial acetic acid and the acenaphthenone-1-spiro-(2:4')-2',3'(CO),6',5'(CO)-dibenzoylene-1',4'-dihydropyridine (V, R = C_6H_5) is formed. It is a red crystalline substance with m.p. 350°, insoluble in alkalies.

The reaction is more difficult with ammonia. When the acenaphthenone-spiro-dibenzoylenepyran is heated with ammonium hydroxide in a sealed tube, only a small amount of the orange acenaphthenone-1-spiro-(2:4')-2',3'(CO),6',5'(CO)-dibenzoylene-1',4'-dihydropyridine (V, R=H) is formed. Excellent results are obtained when the acenaphthenone-1-spiro-dibenzoylenepyran is treated with liquid ammonia in a sealed tube at room temperature. Here large red crystals of the acenaphthenone-spiro-dibenzoylenedihydropyridine, containing one molecule of ammonia, are formed. These red crystals are readily soluble in organic solvents and slightly soluble in water. When recrystallized they lose ammonia and are transformed into the considerably less soluble orange acenaphthenone-spiro-dibenzoylenedihydropyridine.

With ethylamine, and also with certain other amines, we have not as yet been able to isolate the reaction products with the acenaphthenone-1-spiro-dibenzoylenepyran in pure form. Apparently, the acenaphthenone-spiro-dibenzoylenepyran reacts with greater difficulty with ammonia and amines than do the spiropyrans of the phenanthrene series. Such examples, where the pyran oxygen shows difficult reaction with ammonia and amines, have been mentioned in the literature (for example [5]). On the other hand, it had already been mentioned that the diindandionylacenaphthenone molecule is less stable than the diindandionylphenanthrone molecule; consequently, during reaction the molecule can be more easily cleaved, and in turn the cleavage products can react with the ammonia, which interferes with the isolation of pure substances.

EXPERIMENTAL

Acenaphthenone-1-spiro-(2:4')-2',3'(CO),6',5'(CO)-dibenzoylenepyran (IV). To a filtered solution of 1 g of 2,2-diindandionyl-1-acenaphthenone in hot acetic anhydride was added 2 drops of concentrated sulfuric acid and the mixture heated on the boiling water bath. Large yellow crystals began to separate within 5 minutes. The heating was maintained for 45-50 minutes. After cooling, the crystals were separated, washed first with glacial acetic acid, and then with alcohol. The yield of acenaphthenone-1-spiro-(2:4')-2',3'(CO),6',5'(CO)-dibenzoylenepyran was 0.86 g, or 89.5%. After recrystallization from pyridine – yellow crystals with m.p. 360°. The substance is soluble in nitrobenzene, pyridine, dioxane and chloroform, and difficulty soluble in acetone, benzene, glacial acetic acid, carbon tetrachloride, alcohol and ether. It dissolves in concentrated sulfuric acid with an orange-brown color, which turns green when heated. It is insoluble in aqueous alkali solutions. It does not contain an acetyl group.

Found %: C 82.00; H 2.95. $C_{30}H_{14}O_4$. Calculated %: C 82.19; H 3.20.

A suspension of 1.5 g of the acenaphthenone-spiro-dibenzoylenepyran in 50 ml of 3% alcoholic potassium hydroxide was boiled for 1 hour. The substance gradually went into solution, and the liquid first turned orange, and then red. The mixture was filtered and acidified. Yield 1.4 g. Recrystallization from glacial acetic acid gave tiny colorless crystals of the 2,2-diindandionyl-1-acenaphthenone. The substance dissolved in concentrated sulfuric acid with a green color. Its mixture with the pure diindandionylacenaphthenone did not lower the melting point.

Reaction of the acenaphthenone-spiro-dibenzoylenepyran with aniline. A mixture of 1 g of the acenaphthenone-spiro-dibenzoylenepyran, 2 ml of aniline and 20 ml of glacial acetic acid was boiled for 15 minutes. The substance went into solution and the liquid turned red, after which red crystalline plates began to separate, which after cooling were filtered and washed with alcohol. The yield of the acenaphthenone-1-spiro-(2:4')-2',3'(CO),6',5'(CO)-dibenzoylene-1'-phenyl-1',4'-dihydropyridine (V, R=C_6H_5) was 0.6 g (51.3%). M.p. 350°. Readily soluble in nitrobenzene, chloroform, acetone and pyridine; soluble in benzene, dioxane, and glacial acetic acid; and difficulty soluble in alcohol, ether and carbon tetrachloride. Dissolves in concentrated sulfuric acid with a green color. Insoluble in alkalies.

Found %: N 2.73. $C_{36}H_{19}O_3N$. Calculated %: N 2.72.

Reaction of the acenaphthenone-spiro-dibenzoylenepyran with ammonia. A mixture of 0.2 g of the acenaphthenone-spiro-dibenzoylenepyran and approximately 5 ml of liquid ammonia was sealed in an ampoule and allowed to stand at room temperature. The substance dissolved in the ammonia, and the solution turned dark. The next day large red crystals of the acenaphthenone-1-spiro-(2:4')-2',3'(CO),6',5'(CO)-dibenzoylene-1',4'-dihydropyridine (V, R=H), containing one molecule of ammonia, crystallized from the dark solution.

The ampoule was opened and the ammonia allowed to evaporate. The red crystals were washed with cold water and dried in the air. Yield of substance 0.19 g. Decomposes at 166°. Slightly soluble in water. Evolves ammonia when heated with dilute alkali.

Found %: N 5.68. $C_{30}H_{15}O_3N \cdot NH_3$. Calculated %: N 6.16.

The substance gradually loses ammonia when stored. After 2 days an analysis of the same substance gave only 5.33% nitrogen.

The substance dissolved in acetone and in alcohol with decomposition. Recrystallization from alcohol gave orange needle crystals of acenaphthenone-1-spiro-(2:4')-2',3'(CO),-6',5'(CO)-dibenzoylene-1',4'-dihydropyridine with m.p. 374-376°. Insoluble in water, and evolved ammonia when heated with alkali.

Found %: N 3.13. $C_{30}H_{15}O_3N$. Calculated %: N 3.20.

SUMMARY

2,2-Diindandionyl-1-acenaphthenone, similar to 9,9-diindandionyl-10-phenanthrone, when treated with acetic anhydride in the presence of sulfuric acid cyclizes to acenaphthenone-1-spiro-(2:4')-2',3'(CO), 6'5'(CO)-dibenzoylenepyran. With alcoholic caustic the latter is cleaved back to the original 2,2-diindandionyl-1-acenaphthenone.

When reacted with either ammonia or amines, the oxygen bridge of the acenaphthenone-1-spiro-(2:4')-2',3'(CO),6'5'(CO)-dibenzoylenepyran is replaced by nitrogen with the formation of the acenaphthenone-1-spiro-(2:4')-2',3'(CO),6'5'(CO)-dibenzoylenedihydropyridine or its derivatives.

LITERATURE CITED

[1] G. Ya. Vanag and L. S. Geita, Proc. Acad. Sci. USSR 95, 277 (1954).

[2] G. Ya. Vanag and L. S. Geita, J. Gen. Chem. 26, 511 (1956) (T.p. 539).*

[3] M. Zsuffa, Ber., 43, 2915 (1910).

[4] J. Matei, Ber. 62, 2095 (1929).

[5] R. Damiens and R. Delaby, Chem. Zentr. 1952, 1003.

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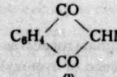
* T.p.= C.B. Translation pagination.

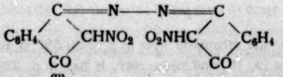
REACTION OF HYDRAZINE HYDRATE WITH 2-NITRO-1,3-INDANDIONE

G. Ya. Vanag and M. A. Matskanova

In the previous paper [1] we had shown that hydrazine with 2-nitro-1,3-indandione (I) in acid solution gives the orange-red azine (II). The reaction proceeds equally well in both water and alcohol solution. A completely different substance is obtained if the nitroindandione in alcohol solution is treated with an excess of hydrazine hydrate. Here a white crystalline compound with m.p. 215° is obtained, in its composition and molecular weight corresponding to the monohydrazone of the nitroindanione. However, the obtained substance does not show the characteristic reactions of hydrazones, for example, it does not condense with either aldehydes or ketones, does not reduce either mercuric oxide or Fehling's solution, and under all conditions does not undergo further change to the nitroindandione azine.

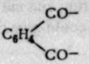


(I)



(II)

After we boiled its solution in glacial acetic acid with zinc dust, the white condensation product gave a positive test for the amino group with bindone [2], from which it follows that the nitro group was retained in the condensation product. The condensation product dissolved in alkalies with a yellow color, and when the solution was acidified it was again precipitated in unchanged form, so that apparently an active hydrogen was retained together with the nitro group. Alkaline solutions of the condensation product did not show change even after prolonged boiling, whereas 1,3-indandione derivatives usually show cleavage to phthalic acid when boiled with alkali for a variable length of time. With resorcinol and concentrated sulfuric acid the condensation product did not give the fluorescein reaction – which the indandione derivatives usually give – also due to cleavage to phthalic acid. However, oxidation of the condensation product with concentrated nitric acid did give phthalic acid. From this it follows that neither the indandione structure nor the phthaloyl rest

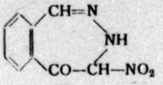


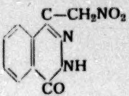
$C_6H_4\begin{smallmatrix}CO-\\CO-\end{smallmatrix}$

is retained as such in the condensation product, but that they are formed again when the condensation product is oxidized.

From all that has been said it is clear that the nitroindandione hydrazone, even if it had been formed initially, showed immediate rearrangement. It is known that the five-membered indandione ring is easily expanded to a six-membered cycle; it is also known that hydrazine, entering into the condensation reaction, frequently effects ring closure, use of which is usually made in the synthesis of pyrazoles, pyrazolines, phthalazones and other heterocyclic systems [3,4].

Since it was difficult to depict such expansion of the indandione ring, where only one nitrogen atom of the nitroindanione hydrazone entered the ring, the rearrangement product was initially assigned a quite unusual formula with a seven-membered ring (III) [5], which, however, on closer study was not justified, and instead proved that the rearrangement product is 1-(nitromethyl)-4-phthalazone (IV):


(III)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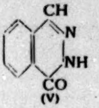
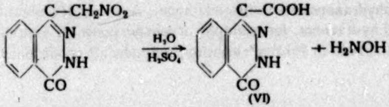

(V)

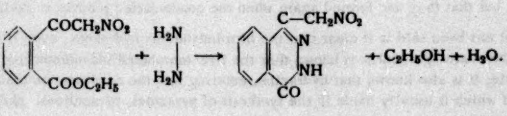
The properties mentioned above for the condensation product do not contradict the nitromethylphthalazone formula. Heating of the latter with dilute sulfuric acid results in cleavage of the nitromethylphthalazone, in which connection nitrogen oxides are evolved and the residue is a gray substance with m.p. 229-230°; when the determination is repeated the m.p. drops to 183-184°. The substance with m.p. 183-184°, also obtained by sublimation of the substance with m.p. 229-230°, and also by its boiling in nitrobenzene, proved to be phthalazone (V).

It is known that the hydrolysis of primary nitro compounds yields carboxylic acids [6-8]. A similar hydrolysis of the nitromethylphthalazone should give the phthalazonecarboxylic acid (VI) and hydroxylamine:

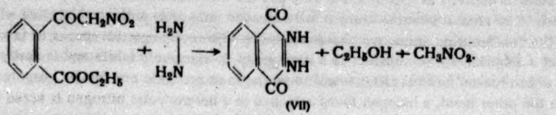

(VI)

It was found that the substance with m.p. 229-230° is actually the phthalazonecarboxylic acid, already described in the literature [9, 10] and, when pure, it has m.p. 232°. The presence of hydroxylamine in the filtrate after boiling with dilute sulfuric acid was also shown. At elevated temperatures the formed phthalazonecarboxylic acid suffers decarboxylation and gives phthalazone (V). For exact identification of the phthalazonecarboxylic acid its ethyl ester was prepared, and also some of its salts. To identify the phthalazone [11] the 3-methylphthalazone was prepared by methylation in alkaline medium, using the method of Gabriel and Neumann [12]. The obtained 3-methylphthalazone had m.p. 112-113°, which failed to correspond to the data of Gabriel and Neumann (102-103°). According to more recent data [13], the melting point of 3-methylphthalazone is 114° (111-112°), which corresponds with the data obtained by us. The other properties of the 3-methylphthalazone are in complete accord with those given in the literature. As a result, the nitromethylphthalazone formula for the reaction product of the nitroindandione with hydrazine hydrate can be considered as having been firmly established.

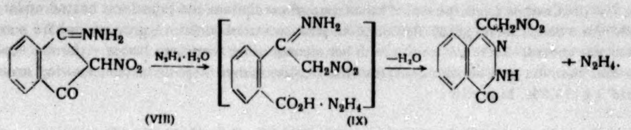
The formation of the nitromethylphthalazone in the indicated reaction could have also been explained as follows. As was shown by L. Zalukaev [14], the treatment of the nitroindandione with ethyl alcohol results in cleavage of its five-membered ring and the ethyl ester of ω-nitroacetophenone-o-carboxylic acid is formed. The latter, reacting with hydrazine, could give the nitromethylphthalazone:



The fact that the nitromethylphthalazone is obtained only in alcohol solution also tends to support this theory; consequently, we ran some experiments on the preparation of the nitromethylphthalazone by reacting hydrazine hydrate with the ethyl ester of ω-nitroacetophenone-o-carboxylic acid. Here it was found that reaction takes place, but instead of the desired nitromethylphthalazone, the phthalhydrazide (VII) was obtained:



From this it is clear that the alcohol does not participate directly in the reaction, and instead only functions as the solvent. The nitromethylphthalazone is formed by the direct reaction of hydrazine hydrate with the nitroindandione, and its whole formation process can be depicted as follows. At first the nitroindandione hydrazone (VIII) is formed, which under the influence of excess hydrazine hydrate, functioning as alkali, cleaves its five-membered ring with the formation of the ω-nitroacetophenone-o-carboxylic acid hydrazone (IX); the latter, cleaving a molecule of water, cyclizes to the nitromethylphthalazone:



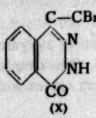
This scheme is also supported by the fact that the best yields are obtained, as can be seen from the Table, if an excess of hydrazine hydrate is taken, and specifically, 2.5 moles of hydrazine hydrate per mole of the nitroindandione. If the reactants are taken in an equimolar ratio, then, in addition to the nitromethylphthalazone, the nitroindandione azine (II) is formed, which not only imparts an orange color to the nitromethylphthalazone, but also lowers the yields. When a larger excess of hydrazine hydrate is used, the yields are also lowered, due in part to the formation of the nitromethylphthalazone hydrazine salt, which, incidentally, decomposes when boiled with water. This salt can also be directly obtained by dissolving the nitromethylphthalazone in excess hydrozine hydrate in alcohol solution.

Preparation of the Nitromethylphthalazone

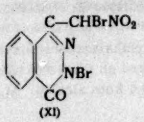
Nitroindandione (g)	Hydrazine hydrate (g)	Molar ratios of the two components	Yields of nitromethylphthalazone	
			(g)	(%)
3.8	1.0	1 : 1	1.5	36.6
3.8	2.0	1 : 2	2.5	61.0
3.8	2.5	1 : 2.5	3.0	73.2
3.8	3.0	1 : 3	2.0	49.0
3.8	4.0	1 : 4	1.0	24.4

Although the nitromethylphthalazone contains a primary nitro group, still it does not give a distinct nitrolic acid test, and only an orange coloration is obtained. The possible reason for this lies in the insolubility of the nitromethylphthalazone in water: the precipitate separates so rapidly that the nitrous acid does not have time to react with it. W. Meister [15] observed a similar phenomenon for a number of water-insoluble nitro compounds.

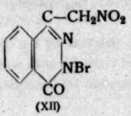
The nitromethylphthalazone is easily brominated, where the dibromonitromethylphthalazone with m.p. 208° is formed, which can be assigned the formula of either (X) or (XI).



(X)



(XI)



(XII)

If the obtained dibromonitromethylphthalazone is suspended in water, then even at room temperature one bromine atom is cleaved as hypobromous acid and the monobromonitromethylphthalazone with m.p. 168-170° is obtained. The second bromine atom is fully cleaved only after prolonged heating with sodium ethylate. The fact that the two bromine atoms are characterized by different properties speaks in favor of formula (XI). It is known that a bromine atom, adjacent to a nitro group, is extremely labile and is easily cleaved as hypobromous acid, for which reason formula (XII) seems to be the most probable one for the monobromonitromethylphthalazone. On the other hand, a halogen found attached to a heterocyclic nitrogen is acted upon only with difficulty by alkali [16, 17].

According to the literature [18], certain phthalazone derivatives are active as antitubercular compounds. From this viewpoint our obtained nitromethylphthalazone and some of its derivatives could be of interest.

EXPERIMENTAL

1-(Nitromethyl)-4-phthalazone (IV). To 3.8 g of the nitroindandione in 100 ml of ethyl alcohol, with vigorous shaking, was added a total of 2.5 g of hydrazine hydrate in drops. Here the pale yellow nitroindandionate hydrazine was obtained as a precipitate. The mixture of precipitate and liquid was heated under reflux in an oil bath at 120° for 3 hours, where, gradually, complete solution was obtained. A gray precipitate was obtained when the solution was cooled. Recrystallization from hot alcohol using acetic or, better, formic acid with the addition of animal charcoal gave slender crystals of the 1-(nitromethyl)-4-phthalazone, showing strong light refraction. Yield 3 g (73.2%). M.p. 215°.

Found %: N 20.36. M 206.20. $C_9H_7O_3N_3$. Calculated %: N 20.45. M 205.17.

A mixture of 1 g of the nitromethylphthalazone and 50 ml of 5% potassium hydroxide was boiled for 2 hours; also a mixture of 1 g of the nitromethylphthalazone and 50 ml of 20% potassium hydroxide was boiled for 4 hours. The pale yellow solutions did not show any apparent change. After acidification the nitromethylphthalazone was recovered, which in its melting point and nitrogen content did not differ from the original substance.

Phthalazonecarboxylic acid (VI). The nitromethylphthalazone (0.3 g) was covered with 30 ml of dilute sulfuric acid and heated on the water bath for 30 minutes. At first complete solution was obtained, and then a small amount of precipitate was formed, which increased in amount when the liquid was diluted with an equal volume of water. The product was filtered and recrystallized from anhydrous alcohol. The yield of the phthalazonecarboxylic acid was 0.22 g, m.p. 229-230°.

Found %: N 14.85. $C_9H_6O_3N_2$. Calculated %: N 14.73.

The sulfuric acid filtrate was found to contain hydroxylamine. This was shown by the fact that it reduces bivalent copper in ammoniacal solution and also by the fact that it shows positive in both the Blom [19] (oxidation of hydroxylamine to nitrous acid) and Berg and Becker [20] (green coloration with 8-hydroxyquinoline) reactions.

Ammonium salt. A solution of the phthalazonecarboxylic acid in anhydrous alcohol was saturated with ammonia. Here the ammonium salt separated as yellow crystals, containing one molecule of crystallization water. M.p. 257-260°.

Found %: N 19.08; H_2O 7.66. $C_9H_9O_3N_3 \cdot H_2O$. Calculated %: N 18.67; H_2O 7.99.

Piperidine salt. An ether solution of piperidine was added in drops to a solution of the phthalazonecarboxylic acid in anhydrous alcohol. The piperidine salt separated as tiny colorless needles. M.p. 237-240° (with decomp.).

Found %: N 15.47. $C_{14}H_{17}O_3N_3$. Calculated %: N 15.26.

Ethyl ester. A mixture of 1 g of the phthalazonecarboxylic acid, 20 ml of anhydrous alcohol, and several drops of concentrated sulfuric acid was heated on the water bath for 6 hours. The excess alcohol was removed by distillation and the residue was recrystallized from alcohol. M.p. 169°, which agrees with the literature [10].

Found %: N 13.11. $C_{11}H_{10}O_3N_2$. Calculated %: N 12.84.

Decarboxylation of the phthalazonecarboxylic acid. One gram of the phthalazonecarboxylic acid was covered with nitrobenzene and boiled for 30 minutes. Here carbon dioxide was evolved. Then the nitrobenzene was steam-distilled and the aqueous residue was evaporated to dryness. The residue was dissolved in 1 ml of boiling water. Cooling gave long transparent needles of phthalazone (V) with m.p. 183°. Yield 0.3 g.

Found %: N 19.17, 19.36. $C_8H_6ON_2$. Calculated %: N 19.17.

The phthalazonecarboxylic acid (0.2 g) was heated in a sand bath. Here the phthalazone sublimed. Yield 0.15 g. The melting point was not depressed when the substance was mixed with authentic phthalazone.

Found %: N 19.09. $C_8H_6ON_2$. Calculated %: N 19.17.

3-Methylphthalazone. A mixture of 0.5 g of the phthalazone, 10 ml of methyl alcohol, 0.5 ml of 40% sodium hydroxide solution, and 1 ml of methyl iodide was heated under reflux for 30 minutes. The methyl alcohol was distilled off and the sirupy residue was stirred with concentrated potassium hydroxide solution. The obtained crystalline slurry was heated until it changed to an oil, which solidified on cooling. The product was washed with ice water and then the 3-methylphthalazone was recrystallized from ethyl acetate. M.p. 112-113°.

Found %: N 17.82. $C_9H_8ON_2$. Calculated %: N 17.50.

Reaction of ethyl ω-nitroacetophenone-o-carboxylate with hydrazine hydrate. To 2 g of the ethyl ω-nitroacetophenone-o-carboxylate in 20 ml of ethyl alcohol was added 1 ml of hydrazine hydrate and the mixture was boiled for 15 minutes, until the whole congealed to a yellow mass. Recrystallization from glacial acetic acid gave the phthalhydrazide (VII) with m.p. 342-345°, which did not depress the melting point when the substance was mixed with pure phthalhydrazide.

Found %: N 17.65. $C_8H_6O_2N_2$. Calculated %: N 17.27.

Dibromonitromethylphthalazone (X or XI). To a solution of 3 g of the nitromethylphthalazone in 100 ml of glacial acetic acid on the water bath was added bromine from a dropping funnel until the solution did not decolorize after several minutes. The excess bromine was removed by blowing with air. Cooling of the solution gave tiny crystals of the dibromonitromethylphthalazone. After recrystallization from either glacial acetic acid or bromobenzene, m.p. 208° (with decomp.). Yield 2 g; an additional amount of the dibromonitromethylphthalazone can be obtained if the first filtrate is evaporated.

Found %: N 11.60; Br 43.98. $C_9H_5O_3N_3Br_2$. Calculated %: N 11.58; Br 44.03.

Monobromonitromethylphthalazone (XII). a) Two grams of the dibromonitromethylphthalazone was covered with 50 ml of water and, with frequent shaking, was allowed to stand for 48 hours. The liquid had a strong hydrobromic acid odor. The precipitate was separated (the filtrate liberates iodine from potassium iodide) and washed with cold water. Recrystallization from glacial acetic acid gave the monobromonitromethylphthalazone with m.p. 168-170°.

Found %: N 14.99; Br 28.76. $C_9H_6O_3N_3Br$. Calculated %: N 14.79; Br 28.66

b) Two grams of the dibromonitromethylphthalazone and 50 ml of water was boiled in a small flask under reflux for 2 hours. The precipitate after cooling was filtered and washed with water. Recrystallization from glacial acetic acid gave 0.8 g of the monobromonitromethylphthalazone with m.p. 168-170°.

Found %: N 14.45. $C_9H_6O_3N_3Br$. Calculated %: N 14.49.

SUMMARY

The reaction of excess hydrazine hydrate with 2-nitro-1,3-indandione in alcohol solution gave 1-(nitromethyl)-4-phthalazone. A mechanism for its formation was given.

Under the influence of dilute sulfuric acid the 1-(nitromethyl)-4-phthalazone was hydrolyzed to the phthalazonecarboxylic acid, the decarboxylation of which gave the phthalazone.

Bromination of the nitromethylphthalazone gave the dibromonitromethylphthalazone. Here one of the bromine atoms is extremely labile and is quickly cleaved as hypobromous acid when treated with water. The remaining bromine atom in the resulting monobromonitromethylphthalazone is fully cleaved only when treated with sodium ethylate.

LITERATURE CITED

[1] G. Ya. Vanag and M. A. Matskanova, J. Gen. Chem. 25, 580 (1955) (T.p. 551).*

[2] G. Vanag, Z. anal. Chem. 113, 21 (1938); 122, 119 (1941); 126, 21 (1943).

[3] V. M. Rodionov and N. G. Yartseva, Reactions and Study Methods of Organic Compounds (State Chemical Press, Moscow-Leningrad, 1951), Vol. I, p. 7.

[4] G. D. Birkit and G. A. Mikhalek, Progr. Chem. 21, 1472 (1952).

[5] G. Vanag, Bull. Acad. Sci. Latvian SSR 1948, No. 8 (13), 56.

[6] V. Meyer and A. Locher, Ann. 180, 163 (1876).

[7] E. Bamberger and E. Rust, Ber. 35, 45 (1902).

[8] J. Houben, Methods of Organic Chemistry (State Chemical Press, 1949), Vol. IV, p. 361.

[9] K. Frankel, Ber. 33, 2808 (1900).

[10] A. Darapsky and P. Heinrichs, J. prakt. Chem. 146, 307 (1936).

[11] V.Paul, Ber. 32, 2014 (1899).

[12] S. Gabriel and A. Neumann, Ber. 26, 521 (1893).

[13] Dictionary of Organic Compounds (1949), III, p. 475.

[14] L. Zalukaev, Bull. Acad. Sci. Latvian SSR 1952, No. 5 (58), 71.

[15] W. Meister, Ber. 40, 3446 (1907).

[16] A. Einhorn and R. Lauch, Ann. 243, 342 (1888).

[17] L. P. Zalukaev, Bull. Acad. Sci. Latvian SSR 1953, No. 11, 111.

[18] N. Buu-Hoi, Compt. rend. 228, 2037 (1949).

[19] J. Blom, Ber. 59, 123 (1926).

[20] K. Berg and B. Becker, Ber. 73, 172 (1940).

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* T. p = C. B. Translation pagination.

NAPHTHALENE SERIES

XIV.* THE LIGHT SENSITIVITY OF AROMATIC SELENIUM-CONTAINING NITRO COMPOUNDS. 1-NITRONAPHTHALENE-8-SELENINIC ACID

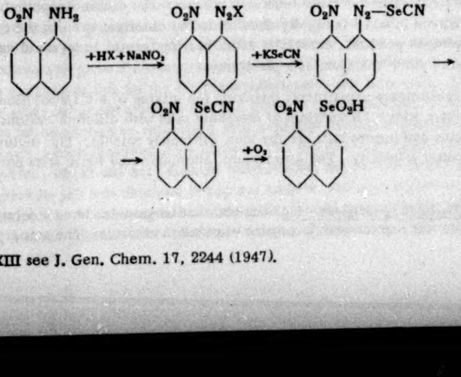
V. V. Kozlov

It had been established earlier [1] that sulfur,substituted α-nitronaphthalene derivatives are frequently characterized by being light-sensitive, and this property is most strongly manifested for certain nitrosulfo-(and disulfo-) acids. It was also established that the appearance of light sensitivity in nitro compounds is strongly dependent on the position of the sulfur-containing group with respect to the nitro group and the structure of the sulfur-containing substituents. Of the investigated nitro compounds of the benzene, naphthalene, anthracene and anthraquinone series,the most sensitive to the influence of sunlight proved to be the peri-nitronaphthalene-sulfonic acid. In an attempt to find even more light-sensitive compounds,we undertook a study of selenium-containing aromatic nitro compounds. Disregarding certain analogies in the properties shown by sulfur and selenium and their compounds, we could assume that selenium-containing compounds might show a certain specificity when exposed to sunlight radiation. Since nothing is known about the light sensitivity of selenium-containing nitrobenzene derivatives, in part described in the literature, we repeated certain syntheses of nitroselenocyanobenzene, nitroselenophenol and dinitrodiphenyl diselenide from the o- and p-nitroanilines [2,3].

The obtained compounds proved to be light-sensitive: o-nitrophenyl selenocyanate with m.p. 138°, o, o'-dinitrodiphenyl diselenide with m.p. 209°, and p,p'-dinitrodiphenyl diselenide with m.p. 183°. Wool samples, impregnated with these compounds in pyridine solution, irreversibly change their color from light yellow to dark yellow when exposed to sunlight. When the behavior of these compounds was compared with that of the corresponding sulfur-containing nitrobenzene derivatives [4],it was found that each pair of analogous compounds shows approximately the same light sensitivity.

Since the peri-nitronaphthalene derivatives, containing either a sulfino or a sulfo group, prove to be the most light-sensitive, we undertook the synthesis of the analogous selenium-containing nitronaphthalene derivatives.

We synthesized the 1-nitronaphthalene-8-seleninic acid by the transformation of diazotized 1-nitro-8-naphthylamine in accord with the scheme:



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* For communication XIII see J. Gen. Chem. 17, 2244 (1947).

The diazotization of the nitronaphthylamine can be run under the usual conditions in hydrochloric acid medium, but for the later reaction with potassium selenocyanate it is necessary to remove all traces of mineral acid by the addition of large amounts of sodium acetate. It proved more convenient to run the diazotization of the nitronaphthylamine in acetic acid solution with dry nitrite, completely avoiding the use of mineral acid. The oxidation of the nitroselenocyanonaphthalene can be realized by prolonged treatment with concentrated nitric acid in concentrated sulfuric acid medium at −10° (by analogy with the nitroselenocyanobenzene [3]), and also by boiling with 20% nitric acid (by analogy with the β-selenocyanonaphthalene [5]). From the obtained 1-nitronaphthalene-8-seleninic acid we prepared its salts with metals and with aromatic amines. Aqueous solutions of the nitroseleninic acid and its salts darken when exposed to sunlight. The color of wool fabric, which has been impregnated with an aqueous solution of these substances, dried, and exposed to sunlight for 15 minutes, becomes considerably more intense: the color changes from pale yellow (before light exposure) to reddish dark yellow (after light exposure).

The light-sensitivity value of the 1-nitronaphthalene-8-sulfinic acid on the light-sensitivity scale is 0.5 degree [6], while for the 1-nitronaphthalene-8-seleninic acid it is 1.0 degree.

In their sensitivity to light, the metal salts of the 1-nitronaphthalene-8-seleninic acid are somewhat weaker than the free acid, while the salts with aromatic amines show a considerably greater light sensitivity.

EXPERIMENTAL

Preparation of 1-nitro-8-selenocyanonaphthalene. Nine g of 1-nitro-8-naphthylamine with m.p. 96° was dissolved in 90 ml of 80% acetic acid and diazotized at 8-10° with 3 g of dry nitrite. The filtered solution was slowly added, with stirring, to a solution of 16 g of KSeCN [7] in 40 ml of water; here nitrogen was violently evolved and a brown precipitate formed. The precipitate was filtered, washed with water, and dried in a desiccator. The yield of crude product was 7.4 g (100%), based on the nitroselenocyanonaphthalene. The product was insoluble in water and soluble in alcohol. It crystallize from dilute alcohol as tiny crystals.

Oxidation of 1-nitro-8-selenocyanonaphthalene. A mixture of 4 g of the nitroselenocyanonaphthalene and 120 ml of 20% nitric acid was heated in a flask under reflux for 6 hours on the boiling water bath. Some of the tarry mass did not dissolve and represented unoxidized starting substance. The hot filtered solution on cooling gave a substance which proved to be the 1-nitronaphthalene-8-seleninic acid. Yield 2.14 g (52%), based on the starting 1-nitro-8-selenocyanonapthalene.

Properties of the 1-nitronaphthalene-8-seleninic acid. The substance is difficultly soluble in cold water, and slightly more soluble in hot water. It crystallizes from either water or 50% acetic acid as light-yellow needles, collecting in clumps, with m.p. 198°. It crystallizes from acetic acid as elongated plates.

Found %: H_2O 11.24. $C_{10}H_6(NO_2)SeO_2H \cdot 2H_2O$. Calculated %: H_2O 11.21. Found %: N 5.12; Se 27.32 [8]; C 42.49; H 2.67. $C_{10}H_7O_4NSe$. Calculated %: C 42.2; H 2.45; N 4.92; Se 27.81.

It could be mentioned that the Lassaigne test was not used to show the qualitative presence of nitrogen in the selenium-containing naphthalene compounds, since here the selenide was formed instead of the cyanide.

The substance is easily reduced in hydrochloric acid medium with zinc. The reduction product diazotizes and couples with resorcinol and naphthols to form dyes. Sulfurous acid in acid medium, alcohol or acetic acid on prolonged heating liberates a water-insoluble reduction product – the dinitrodinaphthyl diselenide. The yellow solution of the substance in water is rapidly decolorized by chlorine, even in the cold. Treatment of the substance with 30% hydrogen peroxide, especially under heating, results in its rapid oxidation. Subsequent treatment with sulfurous acid yields selenium as a precipitate.

Salts with metals. Preliminary experiments involving the mixing of a 0.1N solution of ammonium 1-nitronaphthalene-8-seleninate with 0.1N solutions of inorganic salts with different cations established that the calcium, silver, copper, zinc and ferrous salts are the most difficultly soluble. The sodium, potassium and magnesium salts showed better solubility. The ammonium, aluminum and ferric salts proved to be the most soluble.

The calcium salt $[C_{10}H_6(NO_2)SeO_2]_2Ca \cdot H_2O$ was obtained as granules when a solution of the ammonium nitronaphthalene-seleninate was reacted with a solution of calcium chloride. The salt crystallized from 25% aqueous alcohol.

Found %: H_2O 2.82. $C_{20}H_{12}O_8N_2Se_2Ca \cdot H_2O$. Calculated %: H_2O 2.87. Found %: Ca 6.32. $C_{20}H_{12}O_8N_2Se_2Ca$. Calculated %: Ca 6.57.

The aluminum salt $[C_{10}H_6(NO_2)SeO_2]_3Al \cdot 2H_2O$ was obtained as needles when solutions of the ammonium nitronaphthalene seleninate and aluminum sulfate were reacted. The salt crystallized from 40% alcohol.

Found %: H_2O 4.2. $C_{30}H_{18}O_{12}N_3Se_3Al \cdot H_2O$. Calculated %: H_2O 3.93. Found %: Al 3.24. $C_{30}H_{18}O_{12}N_3Se_3Al$. Calculated %: Al 3.07.

The zinc salt $[C_{10}H_6(NO_2)SeO_2]_2Zn \cdot 2.5H_2O$ was obtained by reacting solutions of the ammonium nitronaphthalene seleninate and zinc sulfate. The salt crystallized as yellow needles from 50% alcohol.

Found %: H_2O 6.56. $C_{20}H_{12}O_8N_2Se_2Zn \cdot 2.5H_2O$. Calculated %: H_2O 6.63. Found %: Zn 10.06. $C_{20}H_{12}O_8N_2Se_2Zn$. Calculated %: Zn 10.26.

The copper salt $[C_{10}H_6(NO_2)SeO_2]_2Cu \cdot H_2O$ was obtained by reacting solutions of the ammonium nitronaphthalene seleninate and copper sulfate. The salt crystallized as dark yellow granules from dilute alcohol.

Found %: H_2O 2.81. $C_{20}H_{12}O_8N_2Se_2Cu \cdot H_2O$. Calculated %: H_2O 2.76. Found %: Cu 10.34. $C_{20}H_{12}O_8N_2Se_2Cu$. Found %: Cu 10.12.

The silver salt $[C_{10}H_6(NO_2)SeO_2Ag] \cdot 2.5H_2O$ was obtained by reacting solutions of the ammonium nitronaphthalene seleninate and silver nitrate. The salt crystallized as brown plates from dilute alcohol.

Found %: H_2O 10.1. $C_{10}H_6O_4NSeAg \cdot 2.5H_2O$. Calculated %: H_2O 10.3. Found %: Ag 27.22. $C_{10}H_6O_4NSeAg$. Calculated %: Ag 27.5.

The ferrous salt $[C_{10}H_6(NO_2)SeO_2]_2Fe \cdot 3H_2O$ was obtained by reacting solutions of the ammonium nitronaphthalene seleninate and ferrous sulfate. The salt crystallized as fine needles from 40% alcohol.

Found %: H_2O 8.8. $C_{20}H_{12}O_8N_2Se_2Fe \cdot 3H_2O$. Calculated %: H_2O 7.96. Found %: Fe 9.1. $C_{20}H_{12}O_8N_2Se_2Fe$. Calculated %: Fe 8.97.

The ferric salt $[C_{10}H_6(NO_2)SeO_2]_3Fe \cdot 4H_2O$ was obtained by reacting solutions of the ammonium nitronaphthalene seleninate and ferric chloride. The salt crystallized as plates from 40% alcohol.

Found %: H_2O 7.14. $C_{30}H_{18}O_{12}N_3Se_3Fe \cdot 4H_2O$. Calculated %: H_2O 7.34. Found %: Fe 5.99. $C_{30}H_{18}O_{12}N_3Se_3Fe$. Calculated %: Fe 5.71.

Salts with amines. In a number of cases the treatment of a 0.2N solution of the ammonium nitronaphthalene seleninate with an equimolar amount of the aromatic amine hydrochloride gave a precipitate of the amine salt and nitronaphthalene-seleninic acid. The salts with aniline, o-toluidine and o-anisidine show good solubility and do not precipitate from aqueous solution. The benzidine salt is precipated in small amount, and is a brown product that dissolves when heated. It crystallizes as granules from 50% alcohol. When an excess of benzidine hydrochloride solution was used, a yellow precipitate was obtained, which after 10-15 minutes turned light green under the liquid, then dark green, and when heated, it turned black. The precipitate obtained here was completely insoluble in water. The solution over the precipitate became completely colorless. The reaction is extremely sensitive and gives a distinct brown color with a small amount of substance, as a result of which it can serve as a qualitative test for the 1-nitronaphthalene-8-seleninic acid. The other isomeric nitronaphthaleneseleninic acids do not show such a specific reaction with benzidine. The mixing of a 1.0N solution of the ammonium nitronaphthalene seleninate with α-naphthylamine hydrochloride also gave a small amount of brown colored salt, which dissolved when heated. The use of excess naphthylamine hydrochloride gave a light brown precipitate, which did not dissolve when heated, but instead turned into a tarry mass. The brown colored β-naphthylamine salt was obtained in copious amount, and crystallized as plates with m.p. 84° from either water or 25% alcohol. With an excess of the naphthylamine hydrochloride solution the precipitate turned brick-red in color, and the solution over it became completely colorless. When heated, the precipitate was transformed into a tarry mass.

SUMMARY

1. It was established that such o- and p-seleno-containing nitrobenzene compounds as the nitroselenocyanides and nitroselenides show considerable light sensitivity when exposed to sunlight.

2. 1-Nitronaphthalene-8-seleninic acid and some of its salts were prepared.

3. It was established that the 1-nitronaphthalene-8-seleninic acid is a more light-sensitive substance than its sulfur-containing analog (1-nitronaphthalene-8-sulfinic acid).

LITERATURE CITED

[1] N. N. Vorozhtsov and V. V. Kozlov, Org. Chem. Ind. (USSR), 4, No. 20, 399 (1937).

[2] H. Bauer, Ber. 46, 94 (1913); 48, 507 (1915).

[3] F. Challenger and A. T. Peters, J. Chem. Soc. 1928, 1364; F. Challenger and D. I. James, J. Chem. Soc., 1936, 1609.

[4] N. N. Vorozhtsov and V. V. Kozlov, J. Gen. Chem. 2, 939 (1932).

[5] J. Loevenich, H. Fremdling and M. Föhr, Ber. 62, 2856 (1929).

[6] N. N. Vorozhtsov and V. V. Kozlov, J. Gen. Chem., 7, 996 (1937).

[7] B. L. Bizckenbach, and K. Kellermann, Ber. 58, 790 (1925); W. Muthmann and E. Schroeder, Ber. 33, 1765 (1900).

[8] H. Meyer, Analysis and Structure Determination of Organic Compounds (United Sci. Tech. Press, 1935), 194.

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CATALYTIC REDUCTION OF AROMATIC NITRO COMPOUNDS

VI. THE INFLUENCE OF SOME FUNCTIONAL GROUPS ON THE REDUCTION KINETICS OF THE NITRO GROUP ON SKELETAL NICKEL

V. P. Shmonina and D. V. Sokolsky

N. D. Zelinsky and **A. A. Streltsova**, in studying the reduction of the nitro group in various aromatic nitro compounds on a platinum catalyst, established that the presence of Cl-, OH-, CH_3-, OCH_3-, COOH-groups in the benzene ring is hardly without effect on the reaction rate [1]. According to the data of other authors [2], the para-substituted nitrobenzenes can be arranged in the following order of decrease in the reduction rate on a skeletal nickel catalyst: nitrobenzene >p-CH_3 > p-OH > p-NH_2 > p-ONa > p-COONa > n-$COOCH_3$ > n-$COOC_2H_5$, in which connection the reduction rate for the sodium p-nitrobenzoate is approximately 1/10, and for the ethyl p-nitrobenzoate approximately 1/50, of that shown by nitrobenzene itself. Of the para-substituted nitrobenzenes the p-CN derivative is most rapidly reduced on a colloidal rhodium catalyst [3], and then follow: p-CHO, p-NO_2, p-COOH, p-I, p-Cl, p-Br, nitrobenzene, p-OCH_3 and, finally, the p-NH_2 derivative shows the slowest reduction rate. In their reduction rates, both on nickel and on a rhodium catalyst, the ortho- and meta-derivatives show a different arrangement than do the para-derivatives. To explain the arrangement order shown by nitro compounds in their reduction rates,the authors resorted to data on dipole moments, dielectric constants, induction effects and electrostatic effects. However, the existing experimental material cannot be explained in this manner.

An analysis of the published work and of our experimental data indicates that the mutual influence shown by the atoms and groups of atoms in a molecule under the conditions of heterogeneous catalytic reaction is first reflected in the adsorption capacity shown by nitro compounds, and frequently leads to such essential change in the concentration of the reactants on a catalyst surface that the stage, limiting the reaction course, also changes. Consequently, the influence shown by substituents on the catalytic reduction rate must be considered in association with the relative adsorption of hydrogen and of the substance being reduced on the catalyst surface.

We studied the influence of the COOH-, COONa-, OH-, ONa- and NH_2-groups on the reduction kinetics of the nitro groups in the corresponding para-nitrobenzene derivatives on skeletal nickel catalyst. In studying the reduction kinetics we changed both the experimental temperature and the concentration of the compound being reduced. In addition, we studied the influence of previous deposition of rhodium on the catalyst surface and the introduction of alkali into the reaction mixture. In combination with the data obtained in the potentiometric study of the catalyst, made by the method of [4], the obtained results permit us to judge the concentration of the reacting components on the catalyst surface during reaction.

EXPERIMENTAL

The nitro compounds used for reduction were of c.p. quality, either freshly distilled or recrystallized, and had the constants: nitrobenzene – b.p. 209° (690 mm); p-nitrobenzoic acid – m.p. 240°; p-nitrophenol – m.p. 114°; p-nitroaniline – m.p. 147°. Electrolytic pure hydrogen was used in the reductions, which were run in a "duck" shaken at a rate of 550-600 oscillations per minute; this assured running the reaction in the kinetics region.

The kinetics of the reaction was studied by the hydrogen absorption rate. The potential of the catalyst was measured by the compensation method against a 0.1N calomel electrode. Alcohol (50°) was used as the solvent, and—when the influence of alkali on the reaction course was studied— a 0.1N solution of NaOH in alcohol (also 50°). In the experiments with alkali the p-nitrobenzoic acid and p-nitrophenol were first converted into the sodium salt and sodium phenolate, respectively. The catalyst was prepared by the alkaline leaching of 1 g of a nickel-aluminum alloy containing 33% nickel. The method used to prepare the catalyst and the experimental procedure have been described earlier [5]. The activated skeletal nickel catalyst was made by depositing 0.0019 g of rhodium as the hydrochloride on the catalyst [6].

The kinetics curves for the reduction of the studied nitro compounds on a skeletal nickel catalyst in alcohol (50°) at 25° are shown in Fig. 1. The curve for the reduction of nitrobenzene passes through both a minimum and a maximum. The reaction assumes zero order when the amino group is introduced, and the average hydrogen absorption rate (Table 1) increases from 6.6 to 8.6 ml of hydrogen per minute. The minimum and maximum on the kinetics curve also vanish when either a hydroxyl or carboxyl group is introduced, and here the average rate rises to 8.1 ml in the first case, and decreases to 3.6 ml of hydrogen per minute in the second case. Based on the order of increase in the reduction rate under the given conditions, the nitro compounds can be arranged as follows: p-nitrobenzoic acid < nitrobenzene < p-nitrophenol < p-nitroaniline. However, this order is characteristic only for a temperature of 25°. At 5° the nitrobenzene is reduced at a faster rate than any of the studied substituted derivatives, while at 40° the substituted nitrobenzene derivatives are reduced more rapidly than nitrobenzene itself.

TABLE 1

Temperature	Substance reduced	0.33 g Ni			0.33 g Ni+0.0019 g Rh		
		alcohol (50°)	0.1N NaOH in alcohol (50°)		alcohol (50°)	0.1N NaOH in alcohol (50°)	
		average H_2 absorption rate (in ml/min.)		maximum shift of the catalyst potential (in mv)	average H_2 absorption rate (in ml/min.)		maximum shift of the catalyst potential (in mv)
5°	Nitrobenzene	4.5	1.0	390	3.6	6.7	350
5	p-Nitrobenzoic acid	1.1	0.0	420	1.9	4.6	370
5	p-Nitrophenol	2.4	1.7	200	2.9	5.4	130
5	p-Nitroaniline	3.2	3.8	295	2.1	5.2	240
25	Nitrobenzene	6.6	1.5	390	10.2	14.3	330
25	p-Nitrobenzoic acid	3.6	0.0	430	4.2	7.5	370
25	p-Nitrophenol	8.1	5.4	180	9.2	16.3	130
25	p-Nitroaniline	8.6	6.0	270	5.2	13.1	250
40	Nitrobenzene	7.1	2.0	360	15.8	17.7	335
40	p-Nitrobenzoic acid	7.6	0.0	385	7.7	6.0	345
40	p-Nitrophenol	16.1	9.7	170	14.8	22.5	125
40	p-Nitroaniline	12.9	9.7	270	9.9	18.1	265

Remarks. Weight of substance taken for reduction was 200 mg.

From the data given in Table 2 it can be seen that on unactivated skeletal nickel in neutral aqueous alcohol medium at 25° an increase in the weight of nitrobenzene leads to a decrease in its reduction rate. In the presence of alkali on unactivated catalyst, the nitrobenzene shows considerably slower reduction than in neutral medium. A decrease in the average nitrobenzene reduction rate with increase in its weight is evidently due to the fact that the nitrobenzene, showing good adsorption on skeletal nickel, displaces to a greater or lesser degree, depending on its solution concentration, the hydrogen on the catalyst surface. In alkaline medium, this property of the nitrobenzene is manifested to a greater degree.

The kinetics curve for the reduction of nitrobenzene on unactivated catalyst at 25°, both in neutral medium (Fig. 1) and in the presence of alkali (Fig. 2), passes through a minimum and a maximum, the presence of which, as was shown earlier in studying the reduction of nitrobenzene-aniline intermediate products [5], is evidence that the process proceeds selectively, through the formation and accumulation of nitrosobenzene.

TABLE 2

Influence of the Concentration of the Substance Being Reduced on the Average Hydrogen Absorption Rate on Unactivated Skeletal Nickel

Substance reduced	weight of substance reduced (in mg)	average H_2 absorption rate (in ml/min.)				
		alcohol (50°) at 25°	0.1N NaOH in alcohol (50°)			
			5°	25°	40°	50°
Nitrobenzene	98	8.7	2.3	5.0	8.7	5.6
	204	6.6	1.0	1.5	2.0	0.8
	300	3.2	0.5	0	0	0
p-Nitrobenzoic acid	100	3.2	0.9	2.3	1.9	—
	200	3.6	0	0	0	—
	300	3.6	0	0	0	—
p-Nitrophenol	100	7.5	2.0	5.4	10.0	11.9
	200	8.1	1.7	5.4	9.7	14.5
	300	8.2	2.2	5.5	10.0	13.3
p-Nitroaniline	100	6.0	2.9	6.2	9.0	10.9
	200	8.6	3.8	6.0	9.7	16.6
	300	9.5	3.4	6.1	9.5	14.3

Remarks. Weight of substance taken for reduction was 200 mg.

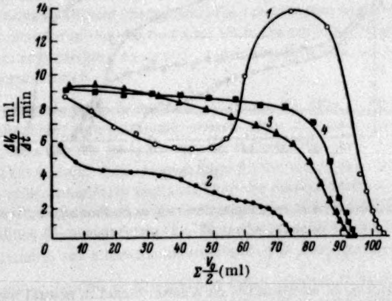

Fig. 1. Reduction of nitrobenzene derivatives on skeletal nickel in alcohol (50°) at 25°. 1) nitrobenzene, 2) p-nitrobenzoic acid, 3) p-nitrophenol, 4) p-nitroaniline.

The deposition of rhodium on the skeletal nickel surface leads to an increase in the average nitrobenzene reduction rate in neutral medium at 25° from 6.6 to 10.2 ml of hydrogen per minute (Table 1) and to a leveling out of the kinetics curve (Fig. 3). It is probable that on the activated catalyst the reduction proceeds without the accumulation of intermediate products.

These data serve as evidence that the quantitative ratio of hydrogen and nitrobenzene on the skeletal nickel surface can be changed by either the addition of alkali or rhodium, in which connection the introduction of alkali increases the nitrobenzene concentration, while the deposition of rhodium increases the amount of hydrogen. The selective nature of the reaction is due to the insufficiency of hydrogen on the catalytic surface. The passage

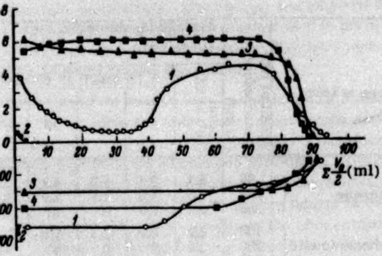

Fig. 2. Reduction of nitrobenzene derivatives on skeletal nickel in 0.1N NaOH solution in alcohol (50°) at 25°. 1) nitrobenzene, 2) sodium p-nitrobenzoate, 3) sodium p-nitrophenolate, 4) p-nitroaniline.

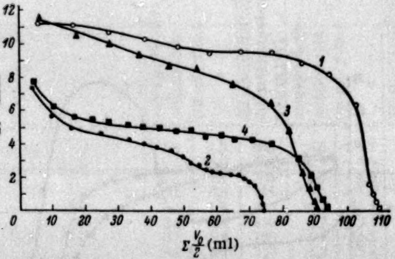

Fig. 3. Reduction of nitrobenzene derivatives on rhodium-activated skeletal nickel in alcohol (50°) at 25°. 1) nitrobenzene, 2) p-nitrobenzoic acid, 3) p-nitrophenol, 4) p-nitroaniline.

of the kinetics curve for the reduction of nitrobenzene on skeletal nickel in neutral medium at 25° through a minimum and a maximum, the reduction in the reaction rate with increase in the amount of nitrobenzene and with the introduction of alkali into the reaction mixture, and also the increase in reaction rate when the catalyst is activated with rhodium, all suggest that under the indicated conditions the reduction of nitrobenzene is limited by the activation of the hydrogen.

The data of Tables 1 and 2 permit following the manner in which the introduction of substituents in nitrobenzene is reflected on the stage limiting the reaction course. An increase in p-nitrobenzoic acid concentration does not effect its reduction rate on skeletal nickel in neutral medium at 25° (Table 2). The deposition of rhodium accelerates the reaction very slightly (Table 1). From this it follows that in the given case, limiting the reaction by activating one of the reactants is not expressed too clearly. The same also holds for the reduction of the p-nitrophenol. An increase in the p-nitroaniline concentration leads to noticeable acceleration of the reaction, while activating the catalyst with rhodium lowers the reduction rate from 8.6 to 5.2 ml of hydrogen per minute.

From this it can be concluded that the reduction of p-nitroaniline is limited by the activation of the reduced substance itself.

In the reduction of the investigated nitrobenzene derivatives, both the minimum and the maximum on the kinetics curves disappear. Consequently, the introduction of substituents liquidates the factor responsible for the selective nature of the reduction process. The probable reason for this is that the introduced substituents make it difficult for the nitro group to be adsorbed on the catalyst surface and in that way reduce its capacity to displace the hydrogen.

Reduction of the experimental temperature to 5° lowers the nitrobenzene reduction rate in neutral medium on unactivated catalyst to 4.5 ml of hydrogen per minute (Table 1). It is characteristic that at this temperature promoting the catalyst with rhodium leads to a decrease in the reduction rate. Here the reaction is limited by the molecular activation of the reduced substance itself; and the introduction of substituents, lowering the adsorption of the nitro compound, retards the reduction rate. Raising the experimental temperature to 40° increases the average nitrobenzene reduction rate to 7.1 ml of hydrogen per minute. At this temperature activating the catalyst with rhodium effects more than a 2-fold increase in the reaction rate. In the given case the reduction is limited by the activation of the hydrogen, and consequently the introduction of the above substituents accelerates the reaction.

As a result, the variable influence shown by the same substituents on the reduction rate of the nitro group on skeletal nickel at various temperatures is conditioned by the change in the stage limiting the reaction course. It is evident that this is due to the fact that the ability shown by the nitrobenzene to displace hydrogen from the catalyst surface increases with increase in temperature.

The introduction of alkali into the reaction mixture lowers the reduction rate on unactivated skeletal nickel for all of the studied nitro compounds at all of the investigated temperatures (Table 1). The kinetics and potentiometric curves for the reduction of the studied nitro compounds on unactivated catalyst in alkaline medium at 25° are shown in Fig. 2. The curve for the reduction of nitrobenzene shows well defined portions of both a minimum and maximum rate. At the start of reaction, the potential of the catalyst shifts by 390 mv in the anode direction and remains without change until the reaction rate begins to rise. A jump in the catalyst potential corresponds to an increase in the reaction rate, while the portion with small changes in the e.m.f. corresponds to the maximum rate portion. As a result, a parallelism is observed here between the course of the kinetics and potentiometric curves.

The introduction of a COONa group in the para-position to the nitro group leads to the situation that the reduction, beginning at a slow rate, soon practically ceases. Here the catalyst potential shows a shift increase of 40 mv. This indicates that a COONa group, in contrast to the COOH group, increases adsorption of the nitro compound on a skeletal nickel surface. The reaction stops for the reason that the hydrogen, capable of reducing the nitro group, proves to be completely displaced from the catalyst surface. If the amount of sodium p-nitrobenzoate is cut in half, then the reduction goes to completion at a rate of 2.3 ml of hydrogen per minute (Table 2), in which connection the kinetics curve has the same shape as for the reduction of nitrobenzene, i.e. it passes through both a minimum and a maximum.

The introduction of either the ONa or NH_2 group in either alkaline or neutral medium leads to a leveling out of the kinetics curve (the reaction becomes zero order) and to a shift decrease of the catalyst potential by 190 and 95 mv, respectively. As a result, the data of the potentiometric study also serve as evidence that the introduction of these groups leads to decreased adsorption of the nitro compound on skeletal nickel.

Based on their reduction rates on unactivated catalyst in alkaline medium at 25° the investigated nitro compounds can be arranged as follows: p-nitroaniline > sodium p-nitrophenolate > nitrobenzene > sodium p-nitrobenzoate. The same order is also retained at 5 and at 40°. This is evidently explained by the fact that in alkaline medium the limiting stage does not change with change in temperature. Based on their reduction rates on rhodium-activated skeletal nickel in neutral medium, the investigated nitro compounds can be arranged in the following order at all three temperatures: nitrobenzene > p-nitrophenol > p-nitroaniline > p-nitrobenzoic acid, i.e. the substituted nitrobenzenes are reduced at a slower rate than nitrobenzene itself. The kinetics curves, taken at 25° (Fig. 3), do not have either a minimum or a maximum. The reaction rate shows comparatively little change in measure with hydrogen absorption, and drops sharply only toward the end. The same influence shown by the substituents at all of the investigated temperatures is explained by the fact that the deposition of rhodium on skeletal nickel leads not only to an increase in the amount of hydrogen adsorbed on the catalyst surface, but also to an increase in the strength of the hydrogen-catalyst bond, as a result of which the nitro compound is unable to displace the hydrogen, even at elevated temperature. In alkaline medium on rhodium-activated catalyst, the reduction rate of all the investigated nitro compounds is considerably higher than in neutral medium (Table 1). In the given case there is double activation: the rhodium increases the amount of active hydrogen adsorbed on the catalyst surface, while the alkali increases the concentration of the nitro compound.

SUMMARY

1. A study was made of the influence shown by the COOH-, COONa-, OH-, ONa- and NH_2-groups on the reduction kinetics of the nitro group in the corresponding nitrobenzene derivatives on skeletal nickel catalyst.

2. In studying the influence of substituents on the catalytic reduction rate, it is necessary to take into consideration the relative adsorption of both the hydrogen and the reduced substance on the catalyst surface.

3. The introduction of COOH-, OH-, ONa- and NH_2-groups in the p-position to the reduced nitro group decreases, and in contrast, the introduction of a COONa group in the same position increases adsorption of the nitro compound on skeletal nickel.

4. The influence of substituents on the reduction rate depends on the quantitative ratio of the hydrogen and nitro compound on the catalyst surface. When the reduction is limited by activation of the hydrogen, then the introduction of groups that reduce adsorption leads to acceleration of the reaction, and based on increase in the reduction rate, the investigated compounds can be arranged in the order: nitrobenzene < p-nitrobenzoic acid < p-nitroaniline < p-nitrophenol. If the reaction is limited by activation of the reduced substance itself, then these same groups exert a hindering action on the reduction rate.

LITERATURE CITED

[1] A. A. Streltsova and N. D. Zelinsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1943, 156.

[2] J. R. Reasenberg, E. Lieber and G. Smith, J. Am. Chem. Soc. 61, 384 (1939); S. Scholnik, J. R. Reasenberg, E. Lieber and G. Smith, J. Am. Chem. Soc. 63, 1192 (1941).

[3] L. Hernandez and F. Nord, J. Colloid Sci. 3, 363 (1948).

[4] D. V. Sokolsky and V. A. Druz, J. Phys. Chem. 26, 364 (1952).

[5] D. V. Sokolsky and V. P. Shmonina, J. Gen. Chem. Suppl. II, 1187 (1953).

[6] V. P. Shmonina and D. V. Sokolsky, J. Gen. Chem. Suppl. II, 1195 (1953).

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EXOMOLECULAR REACTIONS AND COLOR

VI. STUDY OF THE ABSORPTION SPECTRA OF MOLECULAR COMPLEXES OF 1,3-DINITROBENZENE AND 2,4-DINITROSTILBENE WITH DIMETHYLAMINOSTILBENE

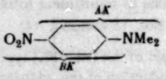
V. A. Izmailsky, A. N. Guseva and E. S. Solovyeva

In the previous communication [1] we described the absorption spectra of the molecular complexes of nitrobenzene and 4-nitrostilbene with 4-dimethylaniline and 4-dimethylaminostilbene. It was shown that the absorption maxima of these complexes (III) and (IV), having the 3 type of structure, lie very close to the absorption maximum of the corresponding compounds in which the nitro and dimethylamino groups are linked by a system of conjugated double bonds: 4-nitrodimethylaniline (I) and correspondingly 4-nitro-4'-dimethylaminostilbene (II), having the 1 type of structure.

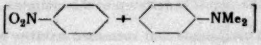
$$\text{Type } 1\text{: } B-\overset{BK}{\underset{AK}{K}}-A. \quad \text{Type } 2\text{: } (B-K)-Q-(K-A).$$

$$\text{Type } 3\text{: } [BK+AK] \text{ or } [BK\frown AK].^{*}$$

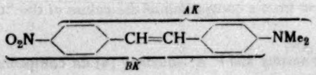
(I)



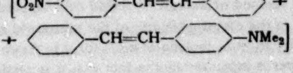
(III)



(II)



(IV)



The color and spectrum of the 1 type of compounds (I) and (II) are determined by endomolecular reaction of the polar chromophores of electron-donor A and electron-acceptor B along the conjugation chain K. In the 3 type of molecular complexes, constructed from the corresponding components AK and BK, present in a molecule of the 1 type, the color and spectrum are determined by exomolecular reaction via an external molecular field.

In our studies we found that we could not limit ourselves to the terms "within" and "between" ("intra" and "inter") for the following reasons. In compounds with unconjugated ("separated") chromophore systems of the 2 type – BK-Q-KA, where Q is a group that breaks the conjugation chain [2], under favorable structural conditions the influence of the external field can be realized not only between separate molecules, but also within molecules.

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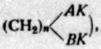
* Here the bow – symbol for conjugation – designates a special type of partial π-bond (exobond) [1, 2].

(for example, by bending of the chain or in the presence of $Q = (CH_2)_4$ or $(CH_2)_5$ [3].

(V) 
$(CH_2)_n\langle^{AK}_{BK}\rangle$, (VI) $BK\frown CH{=}CH\frown KA$, (VII) $BK\frown CH_2\frown KA$.

To emphasize this it seems expedient to use the prefixes exo (external) and endo (internal). As a result, the term "exo" embraces all of the phenomena of complex conjugation (with participation of external molecular exo-forces), arising between the molecules in complexes of the 3-type or in the interior of the molecules in compounds of the 2 type where the chain is bent (V), and together with this a difference is observed from conjugation with participation of internal molecular endo-forces as the result of electron shift along the chain of atoms in a conjugated system where highly polar groups B and A are present (VI), and in compounds of the type of (VII) (see [4], footnote on p. 587, and also [5,6] and [7], p. 221).

In previous communications [1,2] it was shown that by the exomolecular reaction of components AK and BK it is possible to achieve shift effects of the absorption maxima that lie close, and at times exceed those obtained in reaction along the K-chain in a system of the A-K-B type, i.e. in the case where the electrophilic NO_2 chromophore is linked by a compact conjugation chain with the electron-donor NM_2 group in the same molecule.

A comparison of the spectroscopically studied compounds (I) and (II) and the solutions of the corresponding complexes (III) and (IV) revealed that an increase in the magnitude of the conjugated π-electron system enhances the stability of complexes. Thus, for complex (III), even at a concentration of $2 \cdot 10^{-2}$M and a component ratio of 1 AK : 1 BK, only slight reaction is observed, and even with a three-fold excess of one of the components a maximum in the region around 429-430 mμ* does not appear due to strong dissociation of the complex. A maximum can be measured only with a very large excess of the BK component, and specifically, when nitrobenzene is used as a solvent ($\lambda_{max} = 429$ mμ). We obtain a different picture when the styryl radical $-CH{=}CHC_6H_5$ is present in components AK and BK: for complex (IV) even at a component ratio of 1 AK : 1 BK and a concentration of $1 \cdot 10^{-3}$M we observed strong reaction, expressed in the appearance of a maximum at 385 mμ, with a bathochromic shift of +30 mμ with respect to the λ_{max} calculated for the sum of the components (Table 2, Nos. 14 and 17). However, this maximum cannot yet be regarded as being the maximum of complex (IV) and only indicates shifting of the equilibrium $AK + BK \rightleftharpoons [AK\frown BK]$ toward the side of the complex. Only with a three-fold excess of one of the components (a greater concentration increase is impossible due to insufficient solubility) were we able to approach closer to the actual maximum of the complex (Table 2, Nos. 15 and 16).

Further, it was established that increased stability of complexes of the $[AK\frown BK]$ type could be achieved by raising the electron-donor properties of the AK system via the introduction of the additional donor groups $-OCH_3$ and $-NHCOCH_3$ in the para-position. This can be seen from a comparison of the values of the "molar" absorption coefficients** and of the spectral curves [1].

A similar rule was observed earlier by V. A. Izmailsky and P. A. Solodkov [4] for compounds in which the electrophilic chromophore was the imonium group $>C{=}N^{+}<$.

First, it seemed of interest to obtain data supporting the increase in the stability of molecular complexes with increase in the electrophilicity of the nitroenoid system BK via the introduction of an additional nitro group. That the ability to form molecular complexes is shown to a greater degree by dinitro compounds than by mononitro derivatives is supported by the fact that it is possible to isolate the complex of m-dinitrobenzene with dimethylaniline as a crystalline solid, whereas the similar complex with nitrobenzene cannot be isolated [8].

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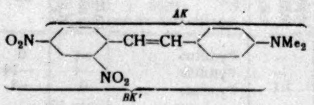
[*] In our paper [1] on page 1411, lines 6 and 9 from the top, the indicated 330 mμ should be 430 mμ. We also take this opportunity to make the following corrections: p. 1408, line 19 from the bottom, the printed "In complex (V)" should be "for complex (V)"; p. 1409, line 14 from the bottom, instead of "piperidine" should be "pyridine"; p. 1414, line 20 from the bottom, the "(V) when compared with (IV)" should be omitted; p. 1413, No. 23, line 32 from the bottom, instead of "420" should be "429".

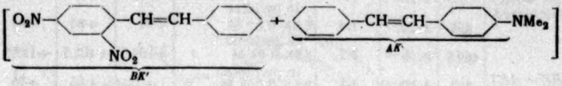
[**] In spectral measurements we actually determine the extinctions corresponding to the equilibrium $AK + BK \rightleftharpoons [AK\frown BK]$ under the given conditions." Due to the fact that in the majority of cases the equilibrium is strongly shifted to the left, the calculated values of the molar absorption coefficients bear a formal character and possess only conditional significance, but still they are extremely helpful in comparing effects.

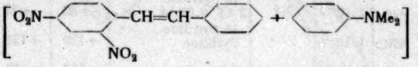
Second, we had in mind to verify on new material for the case of dinitro compounds the observation mentioned above relative to the nearness of the excitation energies in complexes of the [BK⌒AK] type with those of the corresponding conjugated compounds B-K-A.

For this we studied the absorption spectrum of 2,4-dinitro-4'-dimethylaminostilbene (VIII) and compared it with the solution absorption spectra of the molecular complexes [2,4-dinitrostilbene+dimethylaminostilbene] (IX) and [2,4-dinitrostilbene+dimethylaniline] (X).

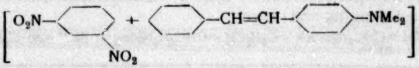
(VIII)


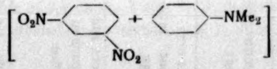
$(B-K'-A)$

(IX)


(X)


Third, to elucidate the influence of the styryl group $-CH=CHC_6H_5$, it seemed desirable to compare the spectra of the 2,4-dinitrostilbene molecular complexes (IX) and (X) with the spectra of the molecular complexes of m-dinitrobenzene with 4-dimethylaminostilbene (XI) and with dimethylaniline (XII).

(XI)


(XII)


The results of the spectroscopic studies are presented in Tables 1 and 2 .

In addition to the 2,4-dinitro-4'-dimethylaminostilbene, we also synthesized both 2,4-dinitrostilbene and 4-dimethylaminostilbene in our study (see Experimental). The absorption spectrum of 2,4-dinitro-4'-dimethylaminostilbene was measured in four solvents. The results of measuring the absorption spectra of (VIII) in ethanol, methanol, benzene and pyridine at a concentration of 10^{-4}M are shown in Fig. 1 and Table 3.

For the long-wave band II in methanol and ethanol a λ^{II}_{max} = 477 mμ is observed. It should be mentioned that in benzene the absorption maximum by direct measurement did not fit in the short-wave portion, as is frequently the case; however, the maxima, calculated from the band half-width, and the limit of adsorption at log ε = 2-3, show hypsochromic shift. Here ε showed unexpectedly strong increase. A fairly strong bathochromic shift was observed in pyridine: Δλ = +23 mμ with respect to the solution in alcohol.

Band I in the short-wave portion has λ^{I}_{max} = 302 mμ. The position of the maximum for I in benzene and in pyridine could not be determined due to the large absorption shown by the solvent itself.

TABLE 1

Comparison of the Absorption Spectra of 2,4-Dinitro-4'-dimethylaminostilbene (VIII) with the Solution Spectra of the Corresponding Complex of the [BK⌒AK] Type (IX)

$BK' = 2,4\text{-}(O_2N)_2C_6H_3CH{=}CHC_6H_5$; $AK = C_6H_5CH{=}CHC_6H_4NMe_2$

Solution No.	Dissolved substance	λ_{max} (in mμ)	Concentration (in M)	Molar component ratio AK:BK	Solvent and comparison solution	Shift $\Delta\lambda_{max}$ in mμ with respect to:		
						calculated sum of BK′+AK	*BK′*	*AK*
1	*BK′*	368	$1\cdot10^{-4}$	—	Pyridine	+8	0	—
2	*AK*	356	$1\cdot10^{-4}$	—	Pyridine	—4	—14	0
3	(*BK′*+*AK*) (IX)	360	$1\cdot10^{-4}$	1:1	Pyridine	0	—8	+4
4	(*BK′*+*AK*) Calculated	452.5	$4\cdot10^{-3}$	1:3	2 BK 0.008 M in pyridine	+92.5	+84	+96.5
5	[*BK′*⌒*AK*]	454	$1\cdot10^{-2}$	1:3	2 BK 0.02 M in pyridine	+94	+86	+98
6		469.5	$2\cdot10^{-2}$	1:3	2BK 0.04 M in pyridine	+109.5	+101.5	+113.5
7		432	$4\cdot10^{-3}$	3:1	2AK 0.008 M in pyridine	+72	+66	+76
8		440	$1\cdot10^{-2}$	3:1	2 AK 0.02 M in pyridine	+80	+72	+84
9	*B—K′—A* (VIII)	490	$1\cdot10^{-2}$	—	Pyridine	+130	+122	+134
10	*B—K′—A* (VIII)	477	$1\cdot10^{-4}$	—	Ethanol	+117	+109	+121

TABLE 2

Comparison of the Absorption Spectra of 4-Nitro-4'-dimethylaminostilbene (II) with the Corresponding Complexes of the [BK⌒AK] Type

$BK = 4\text{-}O_2NC_6H_5CH{=}CHC_6H_5$; $AK = C_6H_5CH{=}CHC_6H_4NMe_2\text{-}4$; $BK'' = m\text{-}C_6H_3(NO_2)_2$

Solution No.	Dissolved substance	λ_{max} (in mμ)	Concentration (in M)	Molar component ratio AK:BK	Solvent and comparison solution	Shift $\Delta\lambda_{max}$ mμ with respect to:		
						calculated sum of BK′ + AK	*BK*	*AK*
11	*BK*	342.5	$1\cdot10^{-4}$		Pyridine	—12.5	0	—
12	*AK*	356	$1\cdot10^{-4}$		Pyridine	—1	+13.5	0
13	*B—K—A* (II)	450.5	$1\cdot10^{-4}$		Pyridine	+95.5	+108	+94.5
14	(*BK*+*AK*) (IV) Calculated	355	$1\cdot10^{-4}$	1 : 1	Pyridine	0	—	—
15	[*BK*⌒*AK*] (IV)	438	$2\cdot10^{-2}$	1 : 3	2 BK 0.04 M in pyridine	+83	+95.5	+82
16		430	$2\cdot10^{-2}$	3 : 1	2 AK 0.04 M in pyridine	+75	+87.5	+74
17		385	$1\cdot10^{-3}$	1 : 1	Pyridine	+30	+42.2	+29
18		~350	$1\cdot10^{-4}$	1 : 1	Pyridine	—5	+ 7.5	— 6
19	[$C_6H_5NO_2$ + +*AK*]	428	$0.94\cdot10^{-4}$	$AK : \infty C_6H_5NO_2$	$C_6H_5NO_2$	—	—	+72
20	[*BK″*⌒*AK*]	421	$1\cdot10^{-2}$	1 *BK″* : 3 *AK*	AK 0.02 M. in pyridine	—	—	+58
21		414	$1\cdot10^{-2}$	3 *BK″* : 1 *AK*	BK 0.02 M in pyridine	—	—	+65
22	BK″	Step ~324	$1\cdot10^{-3}$		Pyridine	—	—	—

TABLE 3

Absorption Spectra of 2,4-Dinitro-4'-Dimethylaminostilbene ($C = 10^{-4}M$)

Expt. No.	Solvent	Band I			Band II		
		λ^{I}_{max} in mμ	ϵ^{I}_{max}	$\log\epsilon^{I}_{max}$	λ^{II}_{max} in mμ	ϵ^{II}_{max}	$\log\epsilon^{II}_{max}$
1	Methanol	302	7410	3.87	476	14 600	4.16
2	Ethanol	302	8520	3.93	477	15 100	4.18
3	Benzene	Could not be determined			480	25 760	4.41
4	Pyridine		"	"	500*	22 400	4.35

* At $C = 10^{-2}M$, λ_{max} = 490 mμ.

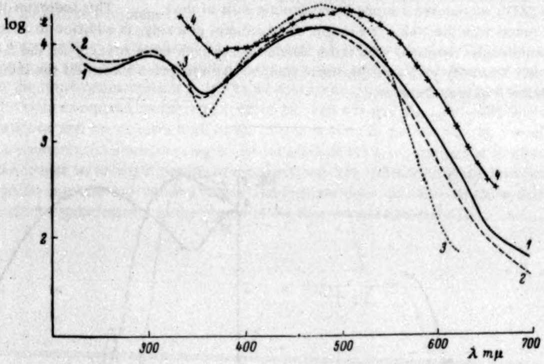
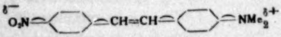
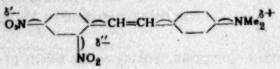


Fig. 1. Absorption spectra of 2,4-dinitro-4'dimethylaminostilbene (VIII) at concentration of 10^{-4}M: in ethanol (1), in methanol (2), in benzene (3), and in pyridine (4).

TABLE 4

№	Substance	Position of λ_{max} (in mμ)	
		in alcohol	in pyridine
(XIII)		450	450.5
(XIV)		477	500 ($C = 10^{-4}$) 490 ($C = 10^{-2}$)

Taking into consideration the fact that in the crystalline state both the color and the spectrum are determined not only by endomolecular, but also by exomolecular forces, we also measured the reflection spectrum of the 2,4-dinitro compound (VIII) (in crystals almost black in color) and compared it with the reflection spectrum of the mononitro compound (II)* (dark brown-red color). Fig. 2 gives a quantitative characterization of the change in color in the solid state when a second nitro group is introduced.

The fact that in solution the 2,4-dinitro compound (XIV) shows considerable bathochromic shift in absorption when compared with the 4-nitro compound (XIII) is of interest from the viewpoint of the theory linking a conjugated structure ("mesostructure") with shifting of the charge along a conjugation chain under light-excitation of the molecule.

From Formula (XIII) in Table 4 we see that the presence of a 2-NO_2 group should cause a reduction in the electron density of the 4-NO_2 group due to the appearance of a shortened conjugated system with involvement of the 2-NO_2 group. Consequently, the fine structure will characterize the electron density distribution between the two nitro groups ("scattering of the electromeric effect," "scattering of the meso effect" [9]). As a result of this in the transition into the excited state the possibility arises of the charge shifting from the NMe_2 group not only along the whole molecule, but also along the shorter system, which should find association with a hypsochromic effect. However, for (XIV) we observe a strong bathochromic shift of the λ_{max}. This indicates that the electrophilic dinitro system reacts with the NMe_2 as a single whole, where, probably, in addition to endomolecular reaction, there is also exomolecular reaction. The latter should appear even more strongly for the 2,4,6-trinitro-4'-dimethylaminostilbene. To verify such a postulation, a study of the absorption spectra of the indicated compounds at a higher concentration is of great interest.

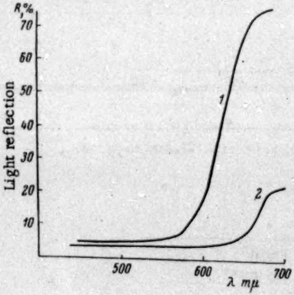


Fig. 2. Light-reflection spectra (% R).
1) 4-nitro-4'-dimethylaminostilbene; 2) 2,4-dinitro-4'-dimethylaminostilbene.

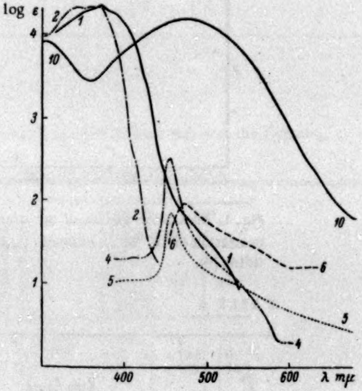


Fig. 3. Absorption spectra of the solutions.
1) 2,4-dinitrostilbene (BK'), 2) 4-dimethylaminostilbene (AK), 4-6) complex [BK' + AK] (IX), and 10) 2,4-dinitro-4'-dimethylaminostilbene (B-K'-A); the curve numbers correspond to Table 1.

From Fig. 3 it can be seen that the maximum absorption, arising as the result of exomolecular reaction in solutions containing the dimethylamino-dinitrostilbene (IX) (Curves 4-6), lies in the absorption region of the corresponding compound with a conjugated system of double bonds between the nitro and dimethylamino groups (XIII) (Curve 10).

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* The reflection spectrum of (II) is taken from the data of P. I. Samokish [5].

We used the method of differential spectroscopy to determine the position of the maximum absorption of our studied molecular complexes. A characteristic maximum is observed at a concentration of about 10^{-2}M and and excess of one of the components, the same as had been described for the complexes of the mononitro compounds [1].

Effect of Introducing the Styryl Radical

By introducing the styryl radical $-CH{=}CHC_6H_5$ we increase the number of π-electrons in a complex chromophore system. Our observations clearly indicate the important part played by the length of the π-electron system not only in conjugated systems of the 1 type, but also in molecules such as AK and BK, forming complexes of the 3 type.

The capacity for complex formation between m-dinitrobenzene and dimethylaniline (XII) is still relatively weakly expressed. As can be seen from Fig. 4 (Curves 24 and 25), the absorption region of the solution at a concentration of 10^{-2}M and a three-fold excess of either component is noticeably shifted to longer waves when compared with the absorption region of the components, which already indicates some interaction of the components under the given conditions. However, here we do not find the maximum characteristic for the complex. To determine the maximum it is necessary to run the measurements at a higher concentration and with a considerably greater excess of one of the components.

When the styryl radical is introduced into component AK (replacement of $C_6H_5NMe_2$ by 4-dimethylaminostilbene) we observe an increase in the stability of the complex with m-dinitrobenzene and a bathochromic shift. Thus, for (XI) at the same concentration of 10^{-2}M we found absorption maxima of 414 mμ ($E_{max} = 2.88$) for the case of excess dinitrobenzene, and molar ratio 1 AK : 3 BK, and 421 mμ ($E_{max} = 0.625$) for the case of excess dimethylaminostilbene, and molar ratio 3 AK : 1 BK (Table 2, Nos. 20 and 21; Fig. 5). In relation to the same for the individual components, the absorption region for solutions of the given molecular complex (XI) is strongly shifted toward the longer wavelength portion of the spectrum: the inflections in the lower branches of Curves 20 and 21 (Fig. 5) go far into the 500-600 mμ region and indicate the appearance of absorption in the 450-540 mμ region, corresponding approximately to the region of the long-wave II band (VIII).

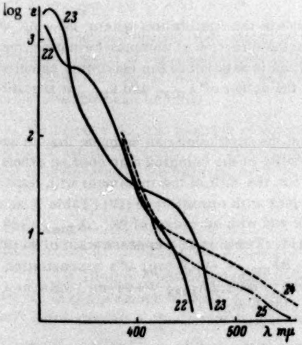

Fig. 4. Absorption spectra of the solutions.
22) m-dinitrobenzene (BK"); 23) dimethylaniline (AK') 24) and 25) complex [BK" + AK] (XII) in pyridine (curve numbers correspond to solution numbers in experimental section).

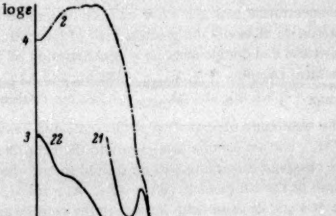

Fig. 5 . Absorption spectra of the solution.
22) m-dinitrobenzene (BK"), 2) 4-dimethylaminostilbene (AK'), 20 and 21) complex [BK" + AK] (XI) (curve nos. correspond to Table 2.

We also observe a further increase in the stability of the complex with absorption shift toward longer waves when the styryl radical is introduced into the BK component, and specifically, when the m-dinitrobenzene is replaced by 2,4-dinitrostilbene. We were able to obtain a more accurate reading for the position of the absorption maximum of complex (IX) by using an excess of one of the components and a molar ratio of 1 AK : 3 BK at a concentration of AK = $2 \cdot 10^{-2}$M: it lies at 470 mμ (469.5 mμ), i.e. in a region close to the region of maximum absorption for the corresponding stilbene compound with a conjugated bond between B and A (VIII) (in alcohol solutions λ^{II}_{max} = 477 mμ). We observe a similar bathochromic shift of the absorption region when the styryl radical is introduced into the $C_6H_5NO_2$(BK) component, i.e. when nitrobenzene is replaced by nitrostilbene. Thus, for the complex composed of two stilbene components (IV) we found that with excess BK, λ_{max} = 438 mμ and that with excess AK, λ_{max} = 430 mμ (Table 2, Nos. 15 and 16). The introduction of a styryl radical into the $C_6H_5NO_2$ molecule gives an even greater effect than when a second nitro group is introduced (replacement of nitrobenzene by m-dinitrobenzene), where we observed maxima at 421 and 414 mμ (Table 2, Nos. 20 and 21).

Effect of Introducing a Second Nitro Group

Further bathochromic shift of the absorption maximum of a complex can be obtained by introducing a second nitro group into the BK component.

When the absorption regions shown by solutions of the corresponding molecular complexes of dimethylaminostilbene with mononitrostilbene (Table 2) and with dinitrostilbene (Table 1) are compared, it can be seen, as was to be expected, that the introduction of a second nitro group into the molecule of the BK component results in bathochromic shift of the absorption maximum (due to increased electrophilicity of the BK component).

The introduction of a second nitro group with a simultaneous increase in the magnitude of the conjugated system, i.e. the use of 2,4-dinitrostilbene as the BK component in the complex with 4-dimethylaminostilbene (IX), gave a very strong effect, manifested not only in a deepening of the color, but also in an increase of the stability: the ability to form complexes was observed at considerably lower concentrations. Thus, even at a concentration of $4 \cdot 10^{-3}$M it is possible to establish the formation of a complex and to determine the position of the absorption maximum under the given conditions (λ_{max} = 452.5 mμ with an excess of the dinitrostilbene) (Table 1 and Figs. 3 and 4). When the concentration is raised to $1 \cdot 10^{-2}$M both the position and shape of Curve 5 are very close to that of Curve 4, and the maximum lies in nearly the same place (λ_{max} = 454 mμ). With further increase in the concentration, both the curve and the maximum shift toward the long-wave portion of the spectrum. For the solutions, we observed the greatest shift of the maxima in relation to the maxima calculated for the sum of the extinctions and components, at a concentration of $2 \cdot 10^{-2}$M and a component ratio of 1 AK : 3 BK, for both the mononitro complex (IV), λ_{max} = 438 mμ and $\Delta\lambda_{max}$ = + 83 mμ (Table 2, No. 15), and the dinitro complex (XI), λ_{max} = 469.5 mμ and $\Delta\lambda_{max}$ = + 110 mμ (Table 1, No. 6).

The maximum observed under the indicated conditions corresponds to the equilibrium system BK + AK $\rightleftharpoons$ [BK⌒AK], and we assume that the more the equilibrium is shifted in the direction of complex formation, the more the observed maximum will be shifted toward the long-wave portion in relation to the maximum calculated for the sum of the components (BK + AK). As a result, on the basis of the values of λ_{max} and E_{max} it is possible to arrive at some decision with respect to the equilibrium state.

When the data in Tables 1 and 2 are analyzed from this viewpoint, the conclusion can be made that an excess of the nitro component BK proves to be more favorable for the stability of the complex than does an excess of component AK, i.e. of dimethylaminostilbene (see [1], p. 1408). Thus, the shift of the maximum with respect to that calculated for the sum of components (AK + BK) is: for the complex with nitrostilbene (IV) (Table 2) at a concentration of $2 \cdot 10^{-2}$M and with an excess of AK, $\Delta\lambda_{max}$ = +75 mμ and with an excess of BK, $\Delta\lambda_{max}$ = +83 mμ. In a similar manner for the dinitro complex with dinitrostilbene (IX) (Table 1) at a concentration of $4 \cdot 10^{-3}$M and with an excess of AK, $\Delta\lambda_{max}$ = +72 mμ and with an excess of BK, $\Delta\lambda_{max}$ = +92.5 mμ; at a concentration of $1 \cdot 10^{-2}$M and and excess of AK, $\Delta\lambda_{max}$ = +80 mμ, and with an excess of BK', $\Delta\lambda_{max}$ = +94 mμ, while at a concentration of $2 \cdot 10^{-2}$M and an excess of BK', $\Delta\lambda_{max}$ even rises to +109.5 mμ.

Results of Comparing the Spectra of Solutions of (BK + AK) with the Spectra of Compounds of the B-K-A Type

Our experiments revealed that the same factors that operate in ordinary conjugated systems of the B-K-A type also exert an influence on the bathochromic effect found in molecular complexes of the [BK⌒AK] type, i.e.

the electron-donor and electron-acceptor capacities shown by the chromophore components AK and BK, and the length and structure of the π-electron systems. The introduction of the styryl radical, of electron-donor groups in AK, and of nitro groups in BK, all proved favorable.

The capacity shown by BK and AK for complex formation and for bathochromic shift proceeds in approximately the following order:

$$2,4\text{-}(O_2N)_2C_6H_3CH{=}CHC_6H_5 > p\text{-}(O_2N)_2C_6H_3{}^{*} > m\text{-}(O_2N)_2C_6H_3 > \\ > p\text{-}O_2NC_6H_4CH{=}CHC_6H_5 > O_2NC_6H_5.$$

A similar situation was also observed for the molecular complexes of quinolinium salts [2,4, 10].

In these complexes the order is: 1-ethyl-2-styrylquinolinium iodide > 1-ethylquinolinium iodide, and 4-$[p\text{-}Me_2NC_6H_4CH{=}CH]C_9H_6N > 2\text{-}[p\text{-}Me_2NC_6H_4CH{=}CH]C_9H_6N > p\text{-}CH_3CONHC_6H_4NMe_2 > C_6H_5NHC_6H_5 > {} > CH_3OC_6H_4NMe_2 > C_6H_5NMe_2$.

A study of the absorption spectra of molecular complexes revealed that from components AK and BK, found in compounds of the B-K-A type in juxtaposition to each other in compounds with a nitro chromophore (B) (as, for example, in the 4-nitrodimethylaniline, 4-nitro-4'-dimethylaminostilbene and 2,4-dinitro-4'-dimethylaminostilbene molecules), and also in compounds with an imonium chromophore (B), as, for example, in the molecules of the cyanine and hemicyanine dyes (pseudocyanine, 1-ethyl-2-[p-dimethylaminostyryl]-quinolinium iodide, 1-ethyl-4-[p-dimethylaminostyryl]-quinolinium iodide), colored molecular complexes of the [AK⌒BK] type can be obtained with their λ_{max} and ϵ_{max} in a region close to that observed for the corresponding compounds of the B-K-A type [2, 4, 10].

The study made by us supported the fact that endomolecular conjugation of two reacting groups – electron-acceptor B and electron-donor A –, by means of a continuous conjugation chain, is not a necessary condition for obtaining a chromophore system with a definite absorption maximum. In the presence of "strong" A and B, the same optical effect, and at times even greater,** can be obtained via conjugation of the two components AK and BK in the molecular complex, i.e. via exomolecular reaction.

As a result, we come to the conclusion that the absorption region, the "depth of color" which is characterized by the position of the maximum and absorption limits in the long-wave portion of the spectrum, for example, at $\log \epsilon = 2$ or 3), arising as the result of exomolecular reactions (both in molecular compounds of the 3 type and in compounds with "separated" unconjugated chromophore systems of the 2 type [2]), in certain cases can lie very close to the region observed for conjuated systems with the same polar systems AK and BK (or of close structure) found in juxtaposition to each other.

The described observations cannot be the result of mere coincidence. We are inclined to think that some sort of rule appears in our observations: in the transition from the ground to the excited state, the energy values for the conjugated compounds B-K-A and for the molecular complexes containing BK and AK systems of comparable structure can be close.

We believe that the reaction of components AK and BK in a molecular complex is realized by means of a partial π-bond ("exobond"), in which connection the exo-ρ-bond appears to be the most probable, arising as the result of layer association between molecules lying in parallel or nearly parallel planes [3].

EXPERIMENTAL

Synthesis and Characterization of the Compounds

1) 2,4-Dinitro-4'-dimethylaminostilbene. By condensing 2,4-dinitrotoluene with p-dimethylaminobenzaldehyde in the presence of small amounts of piperidine, Dippy and coworkers [12] obtained this compound as nearly black crystals with a metallic greenish luster and having m.p. 181°.

We took 2,4-dinitrophenylacetic acid as our starting substance: tiny colorless needles with m.p. 179-180° (with decomp.). Literature: m.p. 178.5-180° [13], 179° [14].

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[*] Based on the experiments of V. A. Izmailsky and A. V. Belotsvetov [11].

[**] For example, for $[C_6H_5NO_2 + C_6H_5NMe_2]$ $\lambda_{max} = 429$ mμ, and for $p\text{-}O_2NC_6H_4NMe_2$ $\lambda_{max} = 395$ mμ (in pyridine [1].

To a well-mixed mixture of 6.8 g (0.03 mole) of 2,4-dinitrophenylacetic acid and 4.5 g (0.03 mole) of p-dimethylaminobenzaldehyde was added 1 ml of piperidine and the whole was heated in a small flask under reflux in an oil bath at 135-140° for 2 hours. The mixture immediately turned dark red when the piperidine was added. The vigorous evolution of carbon dioxide gas began even at 50-65°. The reaction mass foamed badly and gradually became nearly black, with a reddish-purple cast.

On conclusion of heating, the mixture was treated with boiling water, and then with 50 ml of ethyl alcohol. The alcohol extract was a dark red color, turned slightly cloudy when cooled, but did not deposit crystals. The nearly black residue from the alcohol extraction was recrystallized from dichloroethane. Tiny reddish-brown crystals with a purple cast. M.p. 180-181° (with decomp.). From pyridine it was obtained as coarse, near black crystals with a crystalline greenish luster. As a powder it is purplish-brown. M.p. 180-181°. Readily soluble in acetone, hot dichloroethane and pyridine, forming dark red solutions; difficulty soluble in alcohol and ether.

2) 2,4-Dinitrostilbene. Thiele and Escales (1901) obtained the dinitrostilbene by condensing 2,4-dinitrotoluene with benzaldehyde in the presence of either piperidine or diethylamine [15]. Weisler and Helmkamp (1945) obtained it by heating a mixture of the sodium salt of phenylnitromethane and 2,4-dinitrobenzyl chloride [16].

We obtained the 2,4-dinitrostilbene by heating 11.3 g (0.05 mole) of 2,4-dinitrophenylacetic acid, 6 ml (0.05 mole) of freshly distilled benzaldehyde and 1 ml of piperidine in a small flask under reflux in an oil bath at 160-170°. The carbon dioxide evolution began at 100° and continued for an hour. When water began to condense in the condenser tube (cloudy drops) the temperature was reduced to 140°. The mixture was then heated another 2 hours. The cold melt was treated with hot alcohol, and the brown residue was recrystallized from hot acetic acid. The yield was 7 g of tiny, light-brown needle crystals with m.p. 138-140°. After three recrystallizations from glacial acetic acid the yield of compound was 3.2 g. Tiny brown needles, m.p. 140°. Literature: m.p. 139-140° [15], 143-145° [17], 140° [18].

3) 4-Dimethylaminostilbene was obtained from p-dimethylaminobenzaldehyde and phenylacetic acid [1]. M.p. 147.5-148°.

Study of the Absorption Spectra

A Beckman photoelectric spectrophotometer was used for the spectroscopic measurements, which were made at 10 mμ intervals, and at the places of maxima and inflections – every 1-2 mμ. To the above we will add the following.

1) Study of the Pyridine Solutions of 2,4-Dinitrostilbene (BK') With 4-Dimethylaminostilbene (AK)

No. 1. BK at a concentration of 10^{-4}M; λ_{max} = 368 mμ; E_{max} = 2.52; ϵ_{max} = 25200; log ϵ_{max} = 4.40 (Fig. 3, Curve 1).

No. 2. AK at a concentration of 10^{-4}M; λ_{max} = 356 mμ; E_{max} = 2.30; ϵ_{max} = 23000; log ϵ_{max} = 4.36 [1] (Fig. 3, Curve 2).

No. 3. Calculated sum of the absorptions for AK + BK' in pyridine on the basis of Nos. 1 and 2, concentration 10^{-4}M; λ_{max} = 360 mμ when E_{max} = 4.59; ϵ_{max} = 45950, log ϵ_{max} = 4.66.

No. 4. Solution of complex (IX). 3 BK' : 1 AK at concentration AK = $4 \cdot 10^{-3}$M., BK = $12 \cdot 10^{-3}$M. Solvent and comparison solution: BK in pyridine at a concentration of $8 \cdot 10^{-3}$M, λ_{max} = 452.5 mμ when E_{max} = 1.34, ϵ = 335, log ϵ = 2.52 (Fig. 3).

No. 5. Solution of complex (IX). 3 BK : 1 AK at concentration AK = $1 \cdot 10^{-2}$M., BK = $3 \cdot 10^{-2}$M. Solvent and comparison solution: 2 BK in pyridine at a concentration of $2 \cdot 10^{-2}$M, λ_{max} = 454 mμ when E_{max} = 0.725, ϵ = 72.5, log ϵ = 1.86 (Fig. 3).

No. 6. Solution of complex (IX) at C = $2 \cdot 10^{-2}$M. 3 BK : 1 AK. Solvent and comparison solution: 2 BK in pyridine at a concentration of 0.04M, λ_{max} = 469.5 mμ, E_{max} = 1.85, ϵ = 92.5, log ϵ = 1.97 (Fig. 3).

2) Study of Solutions of m-Dinitrobenzene (BK") and 4-Dimethylaminostilbene (AK). Complex (IX) in Pyridine With a Three-fold Excess of One of the Components (Table 2, Nos. 20 and 21, Fig. 4).

No. 20. Solution of 3 AK + 1 BK" at a BK" concentration in solution of $1 \cdot 10^{-2}$M and that of AK $3 \cdot 10^{-2}$ M. Solvent and comparison solution: AK in pyridine at concentration $2 \cdot 10^{-2}$M, $\lambda_{max} = 421$ mμ, $E_{max} = 0.625$, $\epsilon_{max} = 62.5$; $\log \epsilon_{max} = 1.80$.

No. 21. Solution of 1 AK + 3 BK at an AK concentration in solution of $1 \cdot 10^{-2}$M and that of BK $3 \cdot 10^{-2}$M. Solvent and comparison solvent: BK in pyridine at concentration $2 \cdot 10^{-2}$M, $\lambda_{max} = 414$ mμ, $E_{max} = 2.88$, $\epsilon_{max} = 2.88$, $\log \epsilon_{max} = 2.46$.

3) Study of Solutions of m-Dinitrobenzene (BK") With Dimethylaniline (AK') Complex (XII) in Pyridine.

No. 22. BK" at a concentration of 10^{-3}M. The absorption maximum in pyridine could not be measured due to the large inherent absorption of pyridine itself.* A step (inflection) is observed in the 320-340 mμ region, indicating the presence of a band around 324-326 mμ, $\log \epsilon = 2.64$ (Figs. 4 and 5).

No. 23. Solution AK' at a concentration of 10^{-3}M, $\lambda_{max} = 309$ mμ when E_{max} 1.660, $\epsilon_{max} = 1.660$, $\log \epsilon_{max} = 3.22$, and a wide step, indicating the presence of a second maximum in about the 400 mμ region, $\log \epsilon_{max} = 1.45$ (Fig. 4).

No. 24. Solution 1 AK' : 3 BK" at concentration AK' $1 \cdot 10^{-2}$M., BK" $3 \cdot 10^{-2}$ M. Solvent and comparison solution: BK" in pyridine at concentration $2 \cdot 10^{-2}$M (Fig. 4). Inflection around 430 mμ (at $\lambda = 380$, 400, 420, 440 mμ, $E = 0.990$, 0.302, 0.103, 0.007).

No. 25. The absorption spectrum of a similar solution with an excess of dimethylaniline, 3 AK : 1 BK", could also be measured only in the interval from 360 to 600 mμ. Inflection around 424 mμ (at $\lambda = 380$, 400, 420, 440 mμ, $E = 0.955$, 0.245, 0.073, 0.055). For wave lengths below 360 mμ $E > 2.00$ (Fig. 4).

In both cases (Nos. 24 and 25) the complex was strongly dissociated, so that its formation appears only in the shifting of the lower branch of the curve in the long-wave region, with an inflection, indicating the appearance of absorption also in about the 420-430 mμ region. The maximum expected in about 430-435 mμ region did not appear under these conditions.

SUMMARY

1. The reflection spectrum (as a powder) and the absorption spectra of 2,4-dinitro-4'-dimethylaminostilbene (VIII) were measured: in ethanol λ_{max} 477 mμ, and in pyridine 490 and 500 mμ (depending on the concentration).

2. Using a 3-fold excess of one of the components, a concentration of the order of about $1 \cdot 10^{-2}$ to $2 \cdot 10^{-2}$, and the differential spectrographic method, the position of the absorption maximum for a solution of $[2,4\text{-}(O_2N)_2C_6H_3CH{=}CHC_6H_5 + C_6H_5CH{=}CHC_6H_5NMe_2]$(IX) in pyridine was found to be at 454 and 469.5 mμ (calculated for the sum of the components, 360 mμ). The absorption region of (IX) is extremely close to the absorption region of (VIII).

3. Increasing the electrophilicity by adding a second NO_2 group in the BK compenent, and increasing the conjugation magnitude in the system by introducing $-CH{=}CHC_6H_5$ into BK and AK, raises the stability of a molecular complex of the [BK⌒AK] type and causes bathochromic shift of the spectra. The bathochromic effect in complexes is influenced by the same factors as hold for molecules with a conjugated structure: the electron-donor and electron-acceptor capacities shown by the chromophoric components and the structure of the π-electron systems.

4. Our experiments can be regarded as supporting the conclusion [1,2] that the magnitude of the excitation energy, characterizing the position of the maximum, in the exomolecular reaction of the polar chromo-

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*According to the literature: in alcohol: $\lambda^{I}_{max} = 252$ mμ, $\lambda^{II}_{max} = 298$ mμ [19]; in water $\lambda^{II}_{max} = 305$, $\lambda^{II}_{max} = 241.5$ mμ [20].

phore systems AK and BK can lie in a region close to the magnitude of the energy of excitation in a molecule of the A-K-B type, containing the same or structurally related polar chromophore systems in a conjugated position.

LITERATURE CITED

[1] V. A. Izmailsky and A. N. Guseva, J. Gen. Chem. 24, 1402 (1954) (T.p. 1385).*

[2] V. A. Izmailsky, Transactions of the Eighth Conference on Aniline Dye Chemistry and Practice, Dec. 8-11, 1947 (Acad. Sci. USSR Press, 1950), p. 87.

[3] Ramart-Lucas and B. Grignard, Traite de chimie organique (1936), II, 59.

[4] V. A. Izmailsky and P. A. Solodkov, Proc. Acad. Sci. USSR 60, 587 (1948).

[5] V. A. Izmailsky, Transactions of the Fourth Conference on the Problems of Aniline Dye Chemistry and Practice, Oct. 13-15, 1939 (Acad. Sci. USSR Press, 1941), p. 41.

[6] V. A. Izmailsky, D. K. Surkov and M. A. Volodina, J. Gen. Chem. 13, 348, 834 (1943).

[7] A. V. Belotsvetov and V. A. Izmailsky, J. Gen. Chem. 14, 216 (1944); A. V. Belotsvetov, J. Gen. Chem. 14, 227 (1944).

[8] P. Pfeiffer, Organische Molekulverbindungen (1922) 236.

[9] V. A. Izmailsky, Proc. Acad. Sci. USSR 29, 101 (1940); 91, 1119 (1953).

[10] V. A. Izmailsky and P. A. Solodkov, Proc. Acad. Sci. USSR, 75, 391 (1950).

[11] V. A. Izmailsky, G. V. Alekseeva and R. S. Tsekhansky, Transactions of the Scientific-Technical Conference on the Problems of the Synthesis and Application of Dyes, 1954 (State Chemical Press, 1956), p. 98.

[12] J. Dippy, L. Hogarth, H. Watson and F. Williams, J. Soc. Chem. Ind. 56, 396 (1937); Chem. Zentr. 1938, II, 2111; C. A. 32, 1682 (1938).

[13] Borsche, Ber. 42, 1310 (1909).

[14] J. Dippy and J. Page, J. Soc. Chem. Ind. 55, 190 (1936); Chem. Zentr. 1936, II, 1914.

[15] J. Thiele and R. Escales, Ber. 34, 2343 (1901).

[16] L. Weisler and R. Helmkamp, J. Am. Chem. Soc. 67, 1167 (1945).

[17] Pastak, Bull. soc. chim. [4] 39, 74 (1926).

[18] P. Pfeiffer., Ber. 45, 1815 (1912).

[19] Ramart-Lucas and Wahl, Compt. rend. 196, 1804 (1933).

[20] Doub and Vandenbelt, J. Am. Chem. Soc. 71, 2414 (1949).

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STRUCTURE OF GRAMICIDIN S

IV. FURTHER STUDIES OF ITS COPPER COMPLEXES

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A tautomeric structure for gramicidin S was proposed in one of our earlier communications [1]. In this paper we communicate on the experiments and other facts that we found to contradict this exo-acyl-amidine structure for the antibiotic. The absence of the dipeptide leucyl-valine [2] in the decomposition products of the gramicidin is evidence of this, and also the isolation under careful acidification of the "red" copper complex of the gramicidin (in 96% alcohol) of a compound, also giving a copper complex with a "red" absorption spectrum, and probably corresponding to the monomeric form of the gramicidin, which is not in accord with the earlier proposed tautomeric structure. This leads us to postulate that the structure of the gramicidin dimer can correspond to the structural formula given in [1] (Scheme 1), i.e. an endo-acyl-amidine structure, giving a tripeptide absorption spectrum for the copper complex without utilizing the nitrogen found in the ring (monomer ⇄ dimeric structure).

In the present work we studied the absorption spectra of the copper complexes and made a chromatographic analysis of the reduced and desaminated gramicidin S for the purpose of elucidating the rules associated with a change in the structure of the antibiotic, and we also made an attempt to approach the problem of the hydrolytic influence shown by alkalies and acids under the conditions of forming the copper complexes. We established the formation of a "red" absorption spectrum for the reduced gramicidin, most probably associated with monomerization during the reduction process, which can be depicted by the following scheme:

Dimer		Monomer
valyl-ornithyl-leucyl-1,2-(6-benzyl-3,4-cyclotrimethylene)-piperazide	⟶	valyl-ornithyl-(6-benzyl-3,4-cyclotrimethylene)-piperazide

Since the chromatogram of the reduced gramicidin gives only one spot, then this suggests that in its reduction the gramicidin **does not** show profound change, and here the internal structure is changed only in the direction of the diketopiperazine cycle being transformed into the piperazine and hydrogenated amidine bonds. Distribution chromatography on paper gives: 1) for complete hydrolysis before reduction – ornithine, valine, leucine, phenylalanine and proline; 2) after reduction without hydrolysis – one spot, hardly different from the position occupied by the unreduced gramicidin; and 3) after hydrolysis of the reduced gramicidin the chromatogram shows three spots – valine, leucine and ornithine (but not proline or phenylalanine).

These chromatograms support our scheme for the structure of the gramicidin monomer. The absence of amino acids or of a peptide in the solution from the gramicidin reduction indicates that the tripeptide is not cleaved and as a result of reduction, remains linked in one molecule with the formed piperazine. This compound is probably valyl-ornithyl-leucyl-(6-benzyl-3,4-cyclotrimethylene)-piperazide. The disappearance of the proline and phenylalanine after reduction shows that these amino acids are found in the cyclic portion of the amino acid linkages. The δ-amino group in gramicidin cannot participate in the formation of a copper complex due to its distant position; however, for desaminated gramicidin a shift of the absorption maximum to 540 mμ is observed. Such a position for the maximum is characteristic of hydroxyamino acids; for example, glycyl-glycyl-threonine [3] shows an absorption maximum at 540 mμ instead of at 570 mμ. It is possible that in the desaminated gramicidin the shift is associated with the formation of δ-hydroxy-α-aminovaleric acid, in which connection the appearance of the hydroxy group affects the character of the absorption spectrum. On standing with alkali, the absorption maximum of the desaminated gramicidin, the same as for the starting substance, is shifted and reaches a value of 510 mμ.

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* Deceased.

As a result, here we see again the peculiar behavior shown by gramicidin under the influence of alkali and copper, which without question is associated with the peculiarities of its internal structure. A study of the hydrolysis of gramicidin S to verify the obtained results, revealed that rearrangement takes place under conditions that do not permit ordinary hydrolysis under the influence of either acids or alkalies to take place, and specifically, in the presence of the copper complex (for the case of an alkaline medium).

EXPERIMENTAL

I. Study of the Absorption Spectra of Reduced Gramicidin S

1) Electroreduction of gramididin S.* The reduction method was described earlier [4]. The current density was 0.056 A/cm². The current strength (constant) was 6.8-6.9 A, and the voltage was 10 v (at the electrodes). The temperature of the cathode solution was 15-20°. The duration of reduction was 7 hours. On conclusion of experiment the cathode solution was evaporated in vacuo to completely remove the acetic and hydrochloric acids, and then the reduced gramicidin was precipitated with alkali. The precipitation was repeated twice until a pure substance with m.p. 292° was obtained.

2) Chromatogram of reduced gramicidin. All of the chromatograms were obtained in butanol-water medium. The chromatogram of the reduced gramicidin shows one spot in its distribution coefficient close to that of the original gramicidin itself. R_f of the reduced gramicidin 0.8, and R_f of the starting gramicidin 0.85 (Fig. 1).

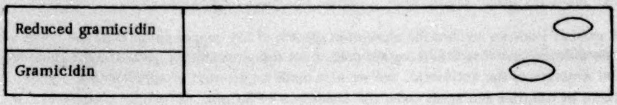

Fig. 1

3) Absorption spectrum of the copper complex of reduced gramicidin. The copper complex of gramicidin was prepared in the usual manner: 0.0486 g of gramicidin was dissolved in 4.8 ml of 4% alcoholic caustic and to the solution was added several drops of a 25% alcoholic solution of cupric chloride until a color appeared. The total volume was 5 ml. The absorption spectrum with a maximum at 535 mμ and absorption intensity ϵ 1.25 remained unchanged on standing and regeneration, which testifies to the stable change of the internal structure (Table 1).

4) Hydrolysis of the reduced gramicidin. A mixture of 0.01 g of reduced gramicidin and 0.5 ml of 22% hydrochloric acid was hydrolyzed in a sealed ampoule for 36 hours at 105°. After hydrolysis three amino acids were found on the chromatogram: ornithine, valine and leucine, and one spot with R_f 0.05. Phenylalanine and proline were absent. [Proline was shown with a 0.4% solution of isatin in butyl alcohol (Fig. 2)].

II. Study of the Absorption Spectra of Desaminated Gramicidin S

It was necessary to establish the effect of eliminating the δ-amino group on the absorption spectra of the copper complexes.

1) Gramicidin S hydrochloride was desaminated according to the V. M. Stepanova method** by the treatment of the gramicidin S base with nitrous acid in acetic acid medium. M.p. 193.5-196.5°. (According to the

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* Done by P. G. Ionisiani.

** The method was developed in our laboratory..

TABLE 1

Absorption Spectrum of Reduced Gramicidin

λ (in mμ)	Value of ε on standing with alkali and copper		λ (in mμ)	Value of ε on standing with alkali and copper	
	original	after 175 hours		original	after 175 hours
450	0.220	0.180	530	1.250	1.230
460	0.300	0.250	540	1.240	1.220
470	0.450	0.380	550	1.150	1.140
480	0.600	0.530	560	1.010	1.010
490	0.800	0.680	570	0.900	0.900
500	0.950	0.850	580	0.800	0.800
510	1.100	1.020	590	0.700	0.700
520	1.200	1.150	600	0.630	0.620
			610	0.550	0.550

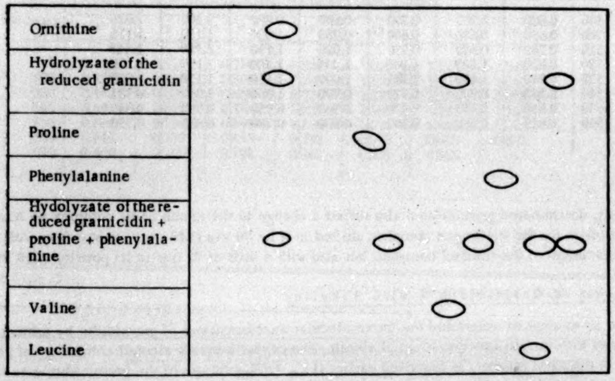

Ornithine
Hydrolyzate of the reduced gramicidin
Proline
Phenylalanine
Hydolyzate of the reduced gramicidin + proline + phenylalanine
Valine
Leucine

Fig. 2

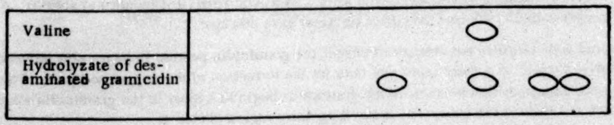

Valine
Hydrolyzate of desaminated gramicidin

Fig. 3

data of V. M. Stepanova, m.p. 195-200°). The substance does not give the ninhydrin reaction and is not developed by ninhydrin when chromatographed on paper. The biuret reaction is positive – a red-purple color (absorption maximum 540 mμ). Chromatographing on paper of the desaminated gramicidin after complete hydrolysis with 20% hydrochloric acid gave 4 spots (Fig. 3), which from their distribution coefficients correspond to proline, valine, phenylalanine and leucine. Here the ornothine spot was completely absent, while that of proline was considerably more intense. This is explained by the transformation of δ-hydroxy-α-aminovaleric acid into proline during hydrolysis with strong hydrochloric acid, as is usually the case for either δ-bromo- or δ-hydroxy-α-amino-valeric acid [5].

2) Preparation of the copper complex of desaminated gramicidin. The substance (0.0986 g) was dissolved in a mixture of 4.8 ml of 50% alcohol, 5 ml of 4% alcoholic caustic solution and several drops of an alcoholic cupric chloride solution. The solution was made up to 10 ml. Desaminated gramicidin has an absorption maximum at 540 mμ and an absorption intensity of $\epsilon = 0.880$. On standing with alkali in the presence of copper the maximum is shifted to 510 m_ϵ (Table 2).

TABLE 2

Effect of Alkali and Copper ($CuCl_2$) on Desaminated Gramicidin

λ (in mμ)	Value of ε after standing (in hours)						
	1	21	28	49	140	after regeneration	406
490	0.600	0.760	0.770	0.860	0.990	1.100	1.025
500	0.650	0.840	0.860	0.960	1.050	1.150	1.115
510	0.740	0.940	0.920	1.020	1.150	**1.200**	**1.160**
520	0.800	**1.000**	**1.000**	**1.110**	**1.200**	1.195	1.120
530	0.840	**1.000**	**1.000**	1.090	1.110	1.150	1.025
540	**0.880**	0.985	0.970	0.990	1.000	1.050	0.935
550	0.860	0.940	0.920	0.900	0.950	0.980	0.845
560	0.840	0.880	0.860	0.800	0.780	0.880	0.750

As a result, desaminated gramicidin S also suffers a change in the nature of its complex on standing with alkali: the maximum for the trinitrogen complex, shifted in it by 30 mμ (540 mμ), on standing with alkali is shifted to the maximum of the finished complex, but also with a shift of 25 mμ in its position (510 mμ).

III. Hydrolysis of Gramicidin S with Alkalies

We made an attempt to understand the intramolecular transformations of gramicidin by subjecting it to careful hydrolysis with various concentrations of alkali. The copper aqueous-alcohol complexes of gramicidin were prepared in the usual manner, as described earlier [1]. 1.0% solutions of the gramicidin were taken for the spectrophotometric measurements.

Effect of 5% alcoholic caustic in the presence and in the absence of copper. The treatment of gramicidin with 5% alcoholic caustic in either the presence or absence of copper resulted in a slow shift of the absorption maximum from longer waves (maximum 560-570 mμ) to shorter waves. After 140 hours the maximum attained a value of 520 mμ and remained at this level even after a very long time (3-4 months) (Table 3). After decomposition of the copper complex the chromatogram on paper gave one spot.

When treated with alkali in the absence of copper, the gramicidin peptide linkages also proceeded to cleave very slowly, but still at a more rapid rate than for the formation of the copper complex. Thus, after 17 days (408 hours), the decomposition products of the gramicidin begin to appear in the gramicidin absorption spectra, evidence of which is a shift of the maximum in the long-wave region (Table 4).

The effect of 10% alcoholic alkali on gramicidin in either the presence or absence of copper is similar to the action of 5% alkali.

Effect of 20% alkali on gramicidin in the presence and in the absence of copper. Similar to the preceding experiments with 5 and 10% alcoholic alkali, a very stable compound is formed in the presence of copper, which fails to decompose even after long standing (45 days and more) (Table 5). After decomposition of the copper complex the chromatogram on paper gave one spot.

TABLE 3

Effect of 5% Alkali in the Presence of $CuCl_2$

λ (in mμ)	Value of ϵ after standing (in hours) with $Cu(OH)_2$							
	1	21	28	49	104	140	280	406
510	0.415	0.760	0.930	0.980	1.080	1.230	1.225	1.120
520	0.475	0.880	1.050	1.050	1.150	**1.250**	**1.245**	**1.200**
530	0.540	0.960	1.100	1.100	**1.200**	1.230	1.220	1.180
540	0.600	1.050	**1.150**	**1.150**	1.150	1.170	1.150	1.162
550	0.649	**1.150**	1.090	1.090	1.100	1.080	1.060	1.020
560	0.681	1.130	1.05	1.040	1.000	0.950	0.940	0.935
570	**0.692**	1.100	1.00	0.980	0.910	0.820	0.805	0.810
580	0.679	1.00	0.920	0.880	0.805	0.680	0.670	0.670

TABLE 4

Effect of 5% Alkali in the Absence of $CuCl_2$

λ (in mμ)	Value of ϵ after standing (in hours) with alkali						
	1	3	24	72	142	260	408
510	0.430	0.510	0.710	0.830	1.025	1.140	1.095
520	0.482	0.550	0.800	0.900	1.100	**1.170**	1.140
530	0.540	0.605	0.850	**0.930**	**1.125**	1.160	**1.165**
540	0.585	0.645	**0.900**	0.920	1.100	1.100	1.125
550	0.605	0.720	0.899	0.870	1.020	1.020	1.050
560	0.645	0.760	0.845	0.830	0.915	0.950	0.975
570	**0.650**	0.755	0.791	0.740	0.845	0.850	—

TABLE 5

Effect of 20% Alkali on Gramicidin in the Presence of $CuCl_2$

λ (in mμ)	Value of ϵ after standing (in hours) with $Cu(OH)_2$									
	1	19	25	53	76	124	153	370	406	1080
510	0.500	0.890	0.950	1.050	1.160	1.115	1.075	1.080	1.200	1.185
520	0.571	0.970	1.050	**1.150**	**1.200**	**1.200**	**1.200**	**1.220**	**1.250**	**1.230**
530	0.675	1.030	**1.100**	**1.150**	**1.200**	1.180	**1.200**	**1.220**	**1.250**	**1.225**
540	0.735	**1.050**	1.080	1.100	1.060	1.100	1.140	1.160	1.200	1.200
550	0.760	0.990	1.000	1.000	0.936	1.00	1.050	1.050	1.100	1.102
560	0.770	0.910	0.905	0.915	0.888	0.900	0.950	0.970	0.985	0.990
570	0.748	0.830	0.805	0.820	0.816	0.750	0.850	0.870	0.875	0.870

When treated with alkali of this concentration in the absence of copper, the substance became unstable, and having at first reached an absorption maximum equal in its character to the curve for the tautomeric form of gramicidin, it began to cleave, in which connection there were successively formed at first tripeptides (λ_{max} 560 mμ), and then dipeptides (λ_{max} 625 mμ) (Table 6).

TABLE 6

Effect of 20% Alkali on Gramicidin in the Absence of $CuCl_2$

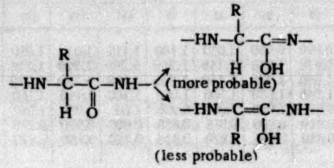
λ (in mμ)	Value of ε after standing (in hours) with alkali							
	15 min.	1	24	44	72	142	370	406
510	0.500	0.735	0.990	0.970	0.889	0.850	0.660	0.580
520	0.570	0.791	**0.998**	1.038	1.000	0.950	0.700	0.650
530	0.675	0.830	0.965	**1.069**	**1.040**	**0.990**	0.765	0.700
540	0.740	**0.845**	0.920	1.065	1.025	**0.990**	0.815	0.760
550	0.765	0.840	0.850	1.030	0.979	0.950	0.855	0.800
560	**0.775**	0.820	0.780	0.955	0.910	0.885	0.875	0.830
570	0.750	0.780	0.705	0.879	0.850	0.785	**0.880**	0.850
580	0.720	0.720	0.600	0.760	0.735	0.700	0.845	**0.855**

IV. Effect of Various Concentrations of Acid on Gramicidin S

In this series of experiments we studied the effect of 5, 10 and 20% acid on gramicidin S. To a known weight of the gramicidin, dissolved in alcohol, was added approximately 5-6 ml of the indicated strength of acid, and the solution was allowed to stand for a definite length of time, after which it was neutralized with 20% alcoholic caustic solution until strongly alkaline. Alcohol was added when a precipitate appeared, and then several drops of an alcoholic solution of cupric chloride, in sucha manner that for the measurements of the absorption spectra, 1% solutions of the gramicidin would be taken. The absorption spectra were measured after the obtained copper complex had stood for an hour.

Effect of 5, 10 and 20% hydrochloric acid. It proved that in all cases the treatment with hydrochloric acid did not effect any changes in the absorption spectra of the gramicidin, and they also did not change with the passage of time, retaining a maximum at 560 mμ. If the hydrochloric acid solutions were made alkaline and allowed to stand with copper salts, then again a shift of the maximum toward shorter wavelengths was observed (λ_{max} 535 mμ).

As a result, the experiments made by us to study the behavior shown by gramicidin in the presence of alkalies and acids support the theory proposed by L. A. Chugaev [6] and M. M. Rising [7], and experimentally established by M. I. Plekhan [8], and I. Nilashi and Ts. Kovach [9], that the formation of the copper complexes is accompanied by enolization of the peptide links from a nitrogen by the following scheme:



From this, the reason for the ease with which diketopiperazines, in contrast to peptides, are hydrolyzed by alkalies becomes quite clear, since such cyclic structures, although they form tautomeric forms similar to the peptides, and do not form copper complexes, are easily hydrolyzed.

SUMMARY

1. In our work it was shown by the absence of their spots on the chromatograms that both proline and phenylalinine are absent in the hydrolyzate of reduced gramicidin, which indicates the presence of a phenylalanylproline diketopiperazine in the molecule.

2. It was found that the shift of the absorption maxima for the copper complexes of both gramicidin and desaminated gramicidin is associated with the presence of a peculiar molecular rearrangement, since after treatment with sodium hydroxide the chromatogram of the regenerated gramicidin corresponds to that of the original substance.

3. The effect of sodium hydroxide in the cold was studied in the presence and in the absence of copper in the complex. It was shown that with various alkali concentrations the copper in the complex stabilizes the gramicidin molecule and protects the peptide link from hydrolysis.

4. It was shown that 5, 10 and 20% hydrochloric acid solutions do not hydrolyze gramicidin in the cold, since here the absorption maximum remains the same, and solid gramicidin can be isolated from solution,since it has the same constants as the original material.

5. Gramicidin, from which the δ-amino group of the ornithine had been removed by desamination, gives with copper in alkaline solutions the same shifting of the absorption maximum of the complex as the original gramicidin, but the absorption maxima of both of the complexes are shifted toward the short-wave side. This establishes that the δ-amino group in the ornithine is free and does not enter into the basic structure of gramicidin.

LITERATURE CITED

[1] L. N. Akimova and N. I. Gavrilov, J. Gen. Chem. 24, 1064 (1954) (T.p. 1063).*

[2] R. Consden, A. H. Grodon and A. J. P. Martin, Biochem. J. 40, 33 (1946); R. Consden, A. H. Gordon, A. J. P. Martin and R. L. M. Synge, Biochem. J. 41, 596 (1947).

[3] M. I. Plekhan, J. Gen. Chem. 22, 1633 (1952) (T.p. 1675).*

[4] P. G. Ionisiani, N. I. Gavrilov and M. I. Plekhan, J. Gen. Chem. 24, 364 (1954) (T.p. 371).*

[5] E. Fischer, Ber. 42, 2989 (1909).

[6] L. A. Chugaev, J. Russ. Chem. Soc. 38, 7 (1907).

[7] M. M. Rising, J. S. Hicks and G. A. Moerke, J. Biol. Chem. 89, 1 (1930); 80, 709 (1928); 99, 755 (1933); J. Am. Chem. Soc. 56, 1178 (1953).

[8] M. I. Plekhan and N. D. Russianova, J. Gen. Chem. 23, 512 (1953) (T.p. 531).*

[9] I. Nilashi and Ts. Kovach, Acta Chim. Acad. Sci. Hung. 2, 45 (1952); 3, 273 (1953); 4, 12 (1954).

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* T.p = C. B. Translation pagination.

CORELBORIN P

M. Ya. Tropp

We had already communicated [1] on obtaining two cardiac glycosides, named, respectively, corelborin K and corelborin P, from two forms – the caucasian and the red – of the domestic hellebore (Helleborus caucasicus A. Br., and H. purpurascens W. et. K.). The pharmacological and clincal testing of these glycosides revealed that in them are combined the basic properties of strophanthin and digitoxin (rapidity of initial effect and duration of action), as a result of which they deserve definite interest in the treatment of cardiovascular diseases [2-4].

We did not observe any essential difference in the biological activity of corelborin K and corelborin P. However, they are different in some of their physicochemical properties and especially in their ability to crystallize (the first gives small needles, and the second gives clumps of round crystals). We classified both of the glycosides as belonging the scillaren group with a six-membered lactone ring [1].

The underground portion of the red hellebore (collected in the fall) is a rich source of corelborin P. The yield of this glycoside reaches 0.1%, whereas the yield of corelborin K from the caucasian hellebore does not exceed 0.02%. As was established by us, the yield of the glycosides is higher when fresh material is used than when dried material is used. For the caucasian hellebore this increase reaches 0.046%, and for the red hellebore – 0.2%.

The red hellebore is easily cultivated. When transplanted from the Carpathian region of the Ukrainian SSR, where it grows wild in the mountains, to the climatic conditions of the Kharkov region (Experimental Station of the Kharkov Scientific-Research Institute of Phamaceutical Chemistry), the red hellebore grafts quite well, whereas the caucasian hellebore is cultivated with greater difficulty under these conditions.

It was also established by us that, in turn, corelborin P can serve as the source of a glycoside comparable to corelborin K, which permits rejecting the use of the caucasian hellebore, which is, indicated above, less rich in the desired glycosides. It should also be mentioned here that the method used to obtain the glycoside from the red hellebore is simpler and economically more feasible than from the caucasian hellebore. For this reason corelborin P is of especial interest.

The chief objective of the present study was to establish the composition of the saccharide portion of corelborin P.

EXPERIMENTAL

It is known that to study cardiac glycosides it is necessary to cleave them into their component parts – agluconic and saccharidic – and study each portion separately. Since corelborin P is difficulty soluble in acetone, it did not seem feasible to use directly the hydrolytic method of Mannich [5] – cleavage with hydrochloric acid in cold acetone solution – as being the most suitable for the cleavage of glycosides under mild conditions (to avoid destruction of the component parts of the natural glycosides). Instead, we proceeded by the enzymatic cleavage route.

We used living enzymes for the cleavage of corelborin P. For this we first used the enzyme prepared from fresh pig liver [6]. Here a sugar was cleaved, which proved to be d-glucose, identified as the glucosazone with characteristic appearance under the microscope and m.p. 203-205°. Its mixture with the osazone from authentic glucose did not depress the melting point. A readily crystallizing substance separated from the fermentation liquor. It showed the properties of a glycoside – reducing Fehling solution only after hydrolysis. The yield of the glycoside was small: it did not exceed 20%. It should be mentioned that obtaining the enzyme preparation from pig liver is an extremely laborious operation and the preparation is unstable when stored. After this we used snail ferment [7] for the cleavage. In our case the ferment proved very effective. Here the yield of the glycoside rose to 65%. We used the fresh pancreatic juice of the snail and also the dry ferment prepared from it, the latter showing enzymatic activity in our experiments even after a year. Such stability for the dry ferment preparation makes its prolonged use possible, whereas the liquid pancreatic juice of the snail can be obtained only in May and June and it can be stored only for a short time (not more than two weeks). It was observed that the solution pH exerts essential influence on the enzymatic cleavage process. The greatest yield of the glycoside was obtained at pH 5.5-5.6. The above data on fermentative cleavage are illustrated by the experimental data summarized in Table 1.

TABLE 1

Fermentative Cleavage of Corelborin P

pH of the medium	Yield of the glycoside (in %)	Ferment
4.7	40.8	Liquid ferment of the snail
5.0	45.2	Liquid ferment of the snail
5.5	64.3	Liquid ferment of the snail
5.6	65.0	Dry ferment of the snail
5.5	66.8	Liquid ferment of the snail
5.2	20	Ferment from pig liver
5.2	17	Ferment from pig liver
5.2	0	Ferment from pig liver after a month's storage

The method recommended for the fermentative cleavage with the pancreatic juice of the snail is as follows. Corelborin P is dissolved in 100 volumes of 50% ethyl alcohol under slight heating and diluted with water to a 1 : 750 dilution. Then to the solution is added 2 volumes, with respect to the taken weight, of fresh juice or the corresponding amount of the dry ferment,* 2 volumes of toluene, and if needed, acetic acid until the pH of the medium is 5.5-5.6. The clear solution is allowed to stand in a thermostat for 4 days at 32-33°, with occasional shaking. Crystals in the form of long needles, collecting as feathery clods, began to appear when the fermentation liquor is reduced to approximately 1/6 of its original volume.

The obtained crystalline precipitate is collected on a fluted filter, washed with water to remove sugar, dried in the air, and then in desiccator. The mother liquor and wash waters are evaporated in vacuo to dryness at a temperature not exceeding 50° (to prevent resinification of the sugar). The residue is treated with anhydrous alcohol to remove protein substances. Traces of the glycoside and sugar go into the alcohol solution. The alcohol solution is evaporated in vacuo to small volume and then diluted with an equal volume of water. The aqueous alcohol liquor is shaken once with 2 volumes of chloroform and 5-7 times with a mixture of alcohol and chloroform (1 : 2) to completely extract the glycoside (Liebermann reaction used as a control).** Most of the glycoside is found in the first two extracts. The subsequent extractions are necessary to completely free the aqueous-alcohol phase, used later to extract the cleaved sugar, from glycoside traces. The combined alcohol-chloroform extracts are washed with water to remove any retained sugar and then dried over anhydrous sodium sulfate. The solvent is vacuum-distilled. The residue is treated with 40% acetone solution until completely dissolved. The aqueous acetone solution is shaken 2-3 times with neutral ether. The colored substances go into the ether. Soon crystals deposit from the acetone-water solution, which are collected on a funnel in vacuo and added to the main product obtained in the evaporation of the fermentation liquor. The obtained substance is recrystallized until the melting point remains constant. Usually one to two recrystallizations are sufficient. The glycoside is always obtained as needle crystals, irrespective of which water-diluted solvent is used for its recrystallization; m.p. 234-241°.

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* Preparation of the dry ferment: fresh pancreatic juice is poured into 5 volumes of anhydrous alcohol, immersed in a Dewar vessel containing liquid oxygen (-80°); the obtained powder is washed with anhydrous alcohol and ether; the dry ferment is stored in the refrigerator in a vacuum-desiccator over calcium chloride.

** One ml of the extract is evaporated to dryness, the residue is dissolved in 0.5 ml of acetic anhydride, and 1-2 drops of concentrated sulfuric acid are added; a blue-green color indicates that glycoside is still present in the extract.

Found %: C 61.63; H 6.75; H_2O 3.00. M 580.4 (lactone titration). $C_{30}H_{42}O_{10} \cdot H_2O$. Calculated %: C 62.05; H 7.68; H_2O 3.10. M 580.6.

In ultraviolet light, an alcohol solution of the glycoside gave an absorption maximum at 3000 A, the same as for corelborin P [1]. This is evidence that a lactone ring with double unsaturation was retained in the isolated glycoside. Its biological activity when tested on the cat was equal to 0.0904 mg/kg of body weight (according to the data of Ya. I. Khadzhai of the Pharmacological Laboratory of the All-Union Scientific Research Institute of Pharmaceutical Chemistry), close to that of corelborin K and corelborin P (0.08-0.1 mg/kg of cat body weight).

Suitable purification of the glycoside-free aqueous-alcohol phase gave a crystalline sugar, which proved to be d-glucose and was identified as the α-methylglycoside with m.p. 162-164°, $[\alpha]_D^{20}$ + 157° (c = 1, water). From the literature the melting point of the α-methylglycoside is 166°, $[\alpha]_D^{20}$ + 158.9°.

Since the glycoside, isolated from the fermentation liquor, in contrast to corelborin P, is soluble in acetone, it could be subjected to acid hydrolysis by the Mannich method. Here a sugar was cleaved, which was obtained in crystalline form and identified as $\underline{1}$-rhamnose from its m.p. 90-92° and $[\alpha]_D^{20}$ +8.8° (after 8-hour standing of the solution; c = 0.75, water), which agrees with the literature for $\underline{1}$-rhamnose: 85-90°, $[\alpha]_D^{20}$ from +8.5 to +9.4°.

From the agluconic portion after chromatographic purification and separation on a column composed of aluminum oxide of the 3rd group of activity according to Brockmann [8] (freed from alkali and reactivated at 180°) we obtained two crystalline substances, which did not reduce Fehling's solution, either before or after hydrolysis. One of them, eluted first from the column with pure chloroform, and also with chloroform containing 0.25-0.5% of methanol, proved to be nonbitter in taste and biologically inactive; the second substance, both bitter and biologically active, was eluted last from the column with chlorform containing 0.75-1% of methanol. These genins, when recrystallized under identical conditions from the same solvent (50% ethanol), differ sharply in their crystal form. It can be seen here that during the hydrolysis process, despite all of the precautions taken (hydrolysis in the cold and using a nitrogen stream), the natural genin suffers partial change, i.e. it becomes inactive. That it is possible to inactivate genins in the process of obtaining them (due to the formation of anhydro compounds) is indicated in the literature [9, 10]. The absorption maxima of the obtained genins proved to be nonshifted. This denotes that also in the inactive genin the lactone ring remains intact. Consequently, the Liebermann reaction also remained positive. However, the bitter taste disappeared and the biological activity dropped to zero. Table 2 illustrates the experiments on the chromatographic separation of the agluconic portion.

The eluates, giving a positive Liebermann reaction, were successively distilled to dryness. The residues were dissolved in either dry methanol or acetone; here instantaneous solution occurred, and crystals separated on standing.

TABLE 2

Chromatographic Separation of Agluconic Portion

Fraction No.	Solvent	Residue after evaporation		Liebermann reaction	Bitter taste
		weight (in g)	melting point		
1-2	Chloroform + benzene	–	–	–	–
3	Chloroform	30	–	–	–
4	Chloroform + 0.25% methanol	170	190-209°	+	–
5	Chloroform + 0.5% methanol	90	173	+	–
6	Chloroform + 0.75% methanol	150	157-165	+	+
7	Chloroform + 1% methanol	200	143-212	+	+
8	"	120	155-210	+	+
9	"	50	146-210	+	+
10	"	0	–	–	–
11	Chloroform + 2% methanol	traces	–	–	–

The 4th and 5th fractions, containing the genin with nonbitter taste, were combined and recrystallized from either methanol or acetone. After recrystallization the melting point rose to 206-209°. Recrystallization of fractions 6-9, containing the bitter genin, gave a preparation with a double melting point of 150 and 212°. Consequently, both genins differ sharply in their crystal form, and in either the presence or absence of a bitter taste, and correspondingly, in either the presence or absence of biological activity. The melting point is not a very highly characteristic value for the active genin.

As a result, we proved that corelborin P is a bioside, in the saccharide portion of which we found without doubt the presence of 1-rhamnose and d-glucose. The data obtained by us agree with the data of Schmutz for hellebrin [11]. Hellebrin is also a bioside, which Schmutz (by enzymatic cleavage with strophanthobiase) was able to decompose to a monoside which he named desglucohellebrin, and d-glucose. Desglucohellebrin, in turn, when subjected to acidic hydrolysis by the Mannich method was cleaved to the genin and 1-rhamnose. Consequently, both the red and black hellebores produce the same glycosides. Apparently, this is explained in part by the fact that the climatic conditions for their growth are extremely alike.

It is possible that both corelborin P and hellebrin are geninic glycosides of primarily plant origin that do not suffer changes under the influence of natural plant enzymes or in the process of their isolation from plants.

SUMMARY

The saccharide component of corelborin P, a cardiac glycoside isolated from domestic raw material (roots and rhizomes of the red hellebore), was studied.

In the enzymatic cleavage of corelborin P with the pancreatic juice of the snail, the first substance to be cleaved is d-glucose, found at the end of the saccharide chain in corelborin P, and a monoside is isolated.

On further acidic hydrolysis the monoside cleaves 1-rhamnose.

LITERATURE CITED

[1] M. Ya Tropp, Yu. V. Shostenko and D. G. Kolesnikov, J. Gen. Chem. 23, 1421 (1953) (T.p. 1489).*

[2] M. A. Angarskaya, Ya. I. Khadzhei and G. N. Maksimenko, Pharmacology and Toxicology 16, No. 5, 46 (1953).

[3] R. I. Sharlai and V. F. Vinokurova, Medical Art 1953, No. 11, 1029.

[4] M. I. Shubov, Clinical Medicine 30, No. 11, 25 (1952).

[5] C. Mannich and G. Siewert, Ber. 75, 737 (1942).

[6] A. Stoll and J. Renz, Helv. Chim. Acta 34, 782 (1951).

[7] H. Huber, F. Blindenbacher, K. Mohr and B. Speiser, Helv. Chim. Acta 34, 64 (1951).

[8] H. Brockmann and H. Schoder, Ber. 74, 73 (1941).

[9] J. Schmutz, Helv. Chim. Acta 32, 1442 (1949).

[10] R. Tschesche and K. Sellhorn, Ber. 86, 54 (1953).

[11] J. Schmutz, Pharm. Acta Helv. 22, 373 (1947).

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* T.p = C. B. Translation pagination.

FRITILLARIA ALKALOIDS

II. THE CHLORINATION PRODUCTS OF RADDEANINE

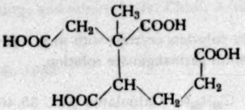
Kh. A. Aslanov and A. S. Sadykov

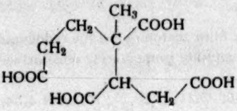
In the previous communication [1] it was shown that raddeanine, the principal alkaloid of F. raddeana, has formula $C_{24}H_{37}N(OH)_2$, is a saturated base, and contains a tertiary nitrogen. The hydroxyl groups bear an alcohol character, but behave differently when acetylated. A similar differential property is also observed in their treatment with phosphorus halides. For example, treatment with phosphorus trichloride gives a compound with the composition $C_{24}H_{37}N(OH)Cl$, which we have named chlororaddeanine, that is apparently formed by the replacement of the tertiary hydroxyl in raddeanine by chlorine.

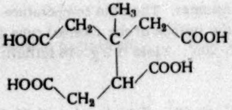
The action of phosphorus pentachloride on raddeanine is characteristic. Here substitution occurs, together with that of the two hydroxyl groups, of one hydrogen atom with the formation of trichlororaddeanine $C_{24}H_{36}NCl_3$. The literature indicates that a similar situation also exists for steriod alkaloids. Thus, the reaction of solanidine with phosphorus pentachloride gave trichlorosolanidine [2]. Raddeanine gives the well known Liebermann reaction, characteristic for steroids and steroid alkaloids.

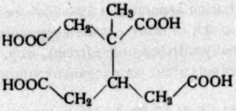
As a result, the theory arose that raddeanine belongs to the class of steroid alkaloids. Such a theory found support in the results of studying the UV-spectrum of raddeanine. It gives a maximum between 280-290 mμ, characteristic for steroid compounds. In its character the absorption curve of raddeanine in the ultraviolet portion of the spectrum is very close to the absorption curves of steroid compounds.

Finally, the oxidation of raddeanine with potassium permanganate in acetone solution gives an acid of composition $C_{10}H_{14}O_8$, the constants of which agree with the constants of the hexanetetracarboxylic acid obtained by the oxidation of the steroid alkaloids cevine and germine [3]. The following formulas (I, II, III, and IV) have been proposed for hexanetetracarboxylic acid:


(I)


(II)


(III)


(IV)

On the basis of the above facts we concluded that raddeanine belongs to the class of steroid alkaloids and, similar to them, and to cholesterol, contains a hydrogenated cyclopentenophenanthrene ring.

It was postulated above that one of the alcoholic hydroxyl groups is tertiary in nature. To prove conclusively the character of the hydroxyl groups we dehydrogenated raddeanine with copper powder. Here we obtained and characterized a crystalline base having the composition $C_{24}H_{35}ON$ (raddeanenone). The base shows ketonic properties: it gives a crystalline oxime with m.p. 210-213°. Distillation of raddeanine hydrochloride in vacuo results in the cleavage of two molecules of water and the formation of an unsaturated base with m.p. 141-142° and composition $C_{24}H_{35}N$, which we have named raddeanidiene. The presented data permit the assertion that raddeanine contains one secondary and one tertiary hydroxyl group.

We are indebted to Yu. N. Sheinker for determining the ultraviolet spectrum of raddeanine.

EXPERIMENTAL

1. Reaction of phosphorus trichloride with raddeanine. To 0.5 g of raddeanine under constant cooling was gradually added 2 g of phosphorus trichloride. After stirring for an hour, another 1 g of phosphorus trichloride was added. The mixture was gradually brought to a boil and kept there for 15 minutes. The excess phosphorus trichloride was distilled on the water bath. The residue, a yellowish powder, was dissolved in water, made alkaline with 15% ammonia, and repeatedly extracted with chloroform. The chloroform solution was washed with water and dried over fused sodium sulfate. Removal of the solvent by distillation gave a powder, the recrystallization of which from acetone with the addition of alcohol gave glistening crystals with m.p. 112-114°. Yield 0.4 g. For the analyses the substance was dried at 80-90° for 2 hours.

Found %: Cl 9.58, 9.63. $C_{24}H_{37}N(OH)Cl$. Calculated %: Cl 9.08.

2. Reaction of phosphorus pentachloride with raddeanine. To a solution of 0.5 g of raddeanine in 10 ml of dry $CHCl_3$ was gradually added 0.7 g of phosphorus pentachloride with vigorous stirring and ice cooling. When all of the phosphorus pentachloride was dissolved and violent reaction had ceased the mixture was boiled under reflux for an hour on the water bath. Then the chloroform was distilled using a water-jet pump and without heating. The residue was dissolved in water and made alkaline with 20% ammonia. Here a white amorphous precipitate was obtained. The latter was separated, washed several times with water, and vacuum-dried (1 mm) at 80-90° for 3 hours. Yield 0.5 g. After recrystallization from methyl alcohol the product had m.p. 199-200°.

Found %: N 3.12, 2.99; Cl 23.64, 23.58. $C_{24}H_{36}NCl_3$. Calculated %: N 3.15; Cl 23.98.

3. Raddeanidiene. To 1 g of raddeanine in 10 ml of acetone was added an acetone solution of hydrogen chloride until acid to Congo, after which the solution was evaporated to dryness. The residue was vacuum-heated (1 mm) at 80-90° for 3 hours. Then the hydrochloride was placed in a vacuum-distillation (1 mm) apparatus and heated at 230-240° for 15 minutes. Here the substance began to distil, and collected on the surface of the internal tube in the apparatus as a glassy mass. The latter was dissolved in weak hydrochloric acid solution and after filtering was made alkaline with 15% ammonia. The resulting precipitate was separated, washed with water, and dried. Yield 0.6 g.

Recrystallization from acetone gave the raddeanidiene as colorless crystals with m.p. 141-142°. The substance in sulfuric acid solution immediately decolorized potassium permanganate solution.

Found %: C 85.00, 85.11; H 10.27, 10.12; N 4.34, 4.37. $C_{24}H_{35}N$. Calculated %: C 85.46; H 10.38; N 4.15.

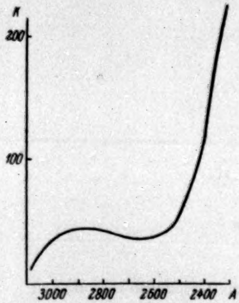
4. Raddeanenone. One gram of raddeanine was mixed with 3 g of copper powder and heated under reduced pressure (5 mm) in a distillation apparatus at 190-200° for 30 minutes. Then the temperature was slowly raised to 300°. Here a certain amount of white powder appeared on the surface of the internal tube in the apparatus, and was collected and recrystallized from alcohol, m.p. 205-206°. Yield 0.2 g. In sulfuric acid solution the product rapidly decolorized potassium permanganate solution.

Found %: C 81.47, 81.37; H 10.08, 10.12; N 4.0, 4.12. $C_{24}H_{35}ON$. Calculated %: C 81.59; H 9.92; N 3.97.

Raddeanenone oxime. To a solution of 0.1 g of raddeanenone in 5% acetic acid was added a mixture of saturated hydroxylamine hydrochloride and sodium acetate solutions (mole for mole) until the colorless flocculent precipitate ceased to form. Then the precipitate was separated and washed several times with acetone. M.p. 210-213° (with decomp.).

5. Hexanetetracarboxylic acid. To 3 g of the base in 30 ml of dry acetone was added 30 g of potassium permanganate dissolved in 200 ml of acetone. After standing for a day the mixture was heated under reflux on the water bath until the permanganate solution was completely decolorized (2-3 hours). Then the precipitate was filtered and washed repeatedly with hot dry acetone, after which it was treated several times with hot water. The aqueous solution, filtered from the manganese dioxide, was acidified with dilute hydrochloric acid solution and extracted with chloroform. After drying and distilling off the solvent the acid was obtained as a yellow powder with m.p. 115-119° (with decomp.). . Yield 0.07 g. After repeated recrystallization from a mixture of acetone and ether it has m.p. 153-157° (with decomp.). The acid is readily soluble in alcohol, acetone, methanol and alkalies, and difficultly soluble in ether, petroleum ether and water.

Found %: C 45.74, 45.62; H 5.38, 5.41. Equiv. 67.10, 67.51. $C_{10}H_{14}O_8$. Calculated %: C 45.80; H 5.34. Equiv. 65.5.



Absorption curve of raddeanine in the ultraviolet portion of the spectrum.

SUMMARY

1. It was shown that raddeanine contains one tertiary and one secondary hydroxyl group.

2. The oxidation of raddeanine gives an acid with the composition $C_{10}H_{14}O_8$, which from its constants coincides with the hexanetetracarboxylic acid obtained in the oxidation of the steroid alkaloids cevine and germine.

3. A study of the UV-spectrum of raddeanine shows that in its character the absorption curve of raddeanine is similar to the absorption curve of steroid alkaloids.

4. On the basis of the obtained data it was postulated that raddeanine belongs to the class of sterioid alkaloids.

LITERATURE CITED

[1] Kh. A. Aslanov and A. S. Sadykov, J. Gen. Chem. 26, 579 (1956) (T.p. 623).*

[2] F. Bergel and R. Wagner, Ber. 67, 446 (1934).

[3] N. Elming, and others, Helv. Chim. Acta 35, 2541 (1952); 36, 2022 (1953).

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FRITILLARIA ALKALOIDS

III. THE STRUCTURE OF RADDEANINE

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In a previous communication [1] it was shown that raddeanine belongs to the class of steroid alkaloids. In the present paper, on the basis of some experimental data supporting the classification of raddianine with the steroid alkaloids, an attempt was made to assign a more probable formula to the structure of raddeanine.

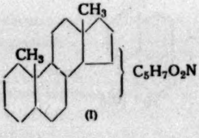
Since all steroids usually contain several C-methyl groups, we decided to determine their amount in raddeanine by a modification of the Kuhn method [2]; here we were able to show that raddeanine contains two C-methyl groups.

The dehydrogenation of raddeanine with selenium was run under various conditions: at 320-340°, in a nitrogen stream, a crystalline base with m.p. 152-153° and composition $C_{22}H_{17}N$ was obtained, giving a picrate with m.p. 203-204° and a hydrochloride with m.p. 92-95°. Dehydrogenation at 370-380° led to the formation of phenanthrene together with the above indicated base, which together with previous data conclusively supports the steroidal character of raddeanine and permits proposing for it the shown Formula (I).

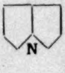
The structure of the heterocyclic portion of the molecule ensues from the following considerations:

1) the nitrogen is tertiary and does not show the $N-CH_3$ group; consequently, the nitrogen is found at the junction of two rings;

2) a pine splinter, moistened with hydrochloric acid, turns red in the vapors of raddeanine, which indicates the presence of either Grouping II or III:



(I)



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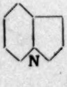

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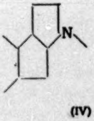
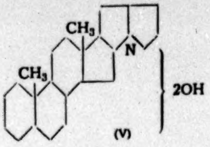


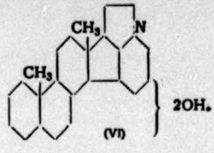
(IV)

Since the (nitrogen-containing) rest of the molecule contains only 5 carbon atoms, it is clear that either ing (II) or (III) is condensed with the hydrocarbon portion of the molecule through either two [in the case of Grouping (II)] or three [(in the case of Grouping (III)] carbon atoms.

Proceeding from these data and taking into consideration the fact that Grouping (IV) is present in many steroid alkaloids, it then becomes possible to postulate only the two Formulas (V) or (VI) for the structure of raddeanine:



(V)

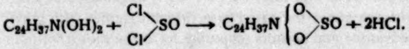


(VI)

A choice between these two formulas can be made only on the basis of the following data. It was shown above that the dehydrogenation of raddeanine with selenium at 320-340° gave a base with composition $C_{22}H_{17}N$. This compound differed from raddeanine in that it did not contain oxygen and showed a smaller number of carbon atoms.

Determination of the $C-CH_3$ group gave a negative result. Consequently, the base $C_{22}H_{17}N$ was obtained from raddeanine by the cleavage of two methyl and two hydroxyl groups with subsequent dehydrogenation. In addition, the base $C_{22}H_{17}N$ was shown to be lacking the pyrrole ring and its pine splinter test was negative. These facts speak in favor of Formula (VI), for Formula (V) does not explain the disappearance of the pyrrole ring during dehydrogenation.

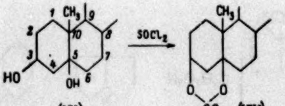
As regards the character and location of the hydroxyl groups, it has already been indicated [1] that raddeanine contains one secondary and one tertiary alcohol hydroxyl. Treatment of raddeanine with thionyl chloride gave a crystalline compound with composition $C_{24}H_{37}O_3NS$, which reverted back to raddeanine when saponified. Consequently, this etherlike compound arises as the cleavage result of two molecules of HCl, derived from the hydrogens of the hydroxyl groups in raddeanine and two chlorine atoms from thionyl chloride:



$$C_{24}H_{37}N(OH)_2 + \begin{matrix} Cl \\ Cl \end{matrix}\!\!>SO \longrightarrow C_{24}H_{37}N\left\{\begin{matrix} O \\ O \end{matrix}\right.\!\!>SO + 2HCl.$$

Such reaction can take place only if both of the hydroxyls are in a row or close to each other.

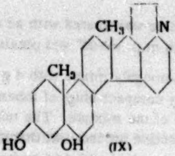
Proceeding from the fact that all steroid alkaloids contain a hydroxyl group in the 3 position, it was postulated that the two hydroxyl groups in raddeanine are found in positions 3 and 5. Such a case the action of thionyl chloride can be explained as follows:



(VII) (VIII)

Such arrangement of the hydroxyl groups is also known for other steroid compounds, which react with thionyl chloride in a similar fashion. Thus, for example, the treatment of strophanthidin [3] with thionyl chloride gives a cyclic ether at the expense of the hydroxyls in the 3 and 5 positions.

As a result, the facts given above make it possible to postulate that the most probable structural formula for raddeanine is (IX):



(IX)

EXPERIMENTAL

1. The C-methyl groups in raddeanine were determined by a modification of the Kuhn method [2]: the oxidation was run in an ordinary flask under reflux.

0.5090 g substance; 0.1030 g CH_3COOH. 0.5112 g substance: 0.1093 g CH_3COOH. Found $C-CH_3$ groups: 1.26, 1.33.

Consequently, raddeanine contains 2 $C-CH_3$ groups.

2. Reaction of thionyl chloride with raddeanine. A solution of 0.5 g of raddeanine in 10 ml of dry chloroform was treated under ice-cooling with a solution of 0.3 g of thionyl chloride in 5 ml of dry chloroform. The mixture was cautiously warmed to room temperature and then filtered. The solvent was removed from the chloroform solution by vacuum-distillation without heating. The residue was dissolved in water and, with strong cooling, was treated dropwise with 20% ammonia solution until alkaline (to phenolphthalein); here a white precipitate formed immediately, which was separated, washed with water, and dried over calcium chloride. Yield 0.55 g. After recrystallization from a mixture of alcohol and water the product had m.p. 192-194°.

Found %: N 3.40, 3.43; S 7.41, 7.28. $C_{24}H_{37}O_3NS$. Calculated %: N 3.34; S 7.64.

3. Saponification of the reaction product of $SOCl_2$ with raddeanine. A solution of 0.3 g of the product in 20 ml of 95% alcohol was treated at the boil with 5 g of metallic sodium in small portions. After all of the sodium had been added the solution was boiled another 25 minutes, then acidified with 20% hydrochloric acid, and the alcohol steam-distilled. The acid solution was made alkaline with 20% ammonia; here a precipitate was obtained, which after recrystallization from alcohol melted at 257-259°.

Its mixture with authentic raddeanine did not depress the melting point. Nor was the mixed melting point of the two perchlorates depressed.

4. Dehydrogenation of raddeanine with selenium. Expt. 1. Twenty grams of powdered selenium metal was thoroughly mixed with ignited asbestos fiber. Sufficient asbestos fiber was taken so that all of the powdered selenium was retained. The selenated asbestos obtained in this manner was impregnated with a saturated solution of 3 g of raddeanine in chloroform, after which the mass was vacuum-dried (5 mm), at first at room temperature and then at 80-90° for 5 hours. The dried mass was placed in the middle of a tube, with a diameter of 15 mm, having a capillary end. Fairly compact plugs of asbestos fiber, each containing about 5 g of metallic selenium, were inserted on each side of the dried mass. The tube was heated for 20 hours at 320-340° with slow passage of a nitrogen stream (1 liter per hour).

Then the tube contents were ground in a mortar and repeatedly extracted with ether. The ether solution was allowed to stand at room temperature; here due to ether evaporation, oily crystals began to appear on the sides of the small Erlenmeyer flask. They were removed mechanically and washed several times with alcohol. In this way 30 mg of crystals was obtained, which after recrystallization from alcohol melted at 152-153°.

Found %: C 89.21, 89.39, H 5.88, 5.97; N 4.81, 4.99. $C_{22}H_{17}N$. Calculated %: C 89.49; H 5.76; N 4.75.

Picrate. When alcohol solutions of the base and picric acid were mixed, the picrate was obtained as a light-yellow powder, which after recrystallization from alcohol melted at 203-204°.

Found %: N 10.99, 10.83. $C_{22}H_{17}N \cdot C_6H_2(OH)(NO_2)_3$. Calculated %: N 10.69.

Hydrochloride. An ether solution of the base was treated with an ether solution of hydrogen chloride; here the completely colorless hydrochloride with m.p. 92-95° was obtained immediately.

Expt. 2. Two grams of raddeanine was thoroughly mixed with 4 g of selenium and placed in a tube with diameter of 1 cm and a length of 40 cm. Fairly compact plugs of asbestos fiber, each containing about 1 g of metallic selenium, were placed on each side of the mixture. The tube was heated at 370-380° for 10 hours with slow passage of a nitrogen stream. The reaction product was thoroughly ground in a mortar and treated several times with ether. The ether solution was washed with 10% hydrochloric acid solution; here an oil separated, insoluble in both ether and water. The oil was separated and washed several times with water. Then it was dissolved in alcohol. The alcohol solution was treated with an alcohol solution of picric acid. The yellow-brown picrate obtained here had m.p. 90-110° (with decomp.). Fractional crystallization from alcohol gave the picrate with a light-yellow color and m.p. 199-201°. Its mixture with the picrate, obtained from the base with m.p. 152-153° and isolated in the preceding experiment, did not show a melting point depression.

The ether was removed from the ether solution by distillation on the water bath. The residue, a thick dark brown oil, was dissolved in a small amount of alcohol, and then a small amount of water was added to the alcohol solution; here cloudiness appeared, but no precipitate. The solution was centrifuged and the supernatant liquor was decanted with a siphon. The residue was washed several times with water by the method of adding water, shaking, centrifuging and decanting the water with a siphon, and, after drying in the air, was vacuum-distilled at 2 mm. The first distillation gave a yellowish powder, impregnated with an oil (110 mg). This powder was vacuum-distilled another 5 times, in which connection the first and last fractions were discarded, and only the middle portion of the distillate was taken. In this way 5 vacuum-distillations gave 11 mg of white lustrous powder with m.p. 97-98°.

Found %: C 94.17, 94.02; H 5.75, 5.80. $C_{14}H_{10}$. Calculated %: C 94.38; H 5.62.

Its mixture with phenanthrene (Kahlbaum quality) did not show a melting point depression.

SUMMARY

1. It was experimentally shown that raddeanine belongs to the class of steroid alkaloids by isolating phenanthrene from the dehydrogenation products of raddeanine with selenium; here, in addition to phenanthrene, a base with composition $C_{22}H_{17}N$ was isolated.

2. The most probable position of the alcohol hydroxyl groups in raddeanine was established by studying the reaction of raddeanine with thionyl chloride.

3. On the basis of the obtained data a formula was proposed for the most probable structure of raddeanine.

LITERATURE CITED

[1] Kh. A. Aslanov and A. S. Sadykov, J. Gen. Chem. 26, 579 (1956) (T.p. 623).*

[2] V. M. Belikov, Progr. Chem. 21, 496 (1952).

[3] P. Plattner and others, Helv. Chim. Acta 30, 1432 (1947).

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* T.p= C. B. Translation pagination.

DELPHINIUM ALKALOIDS

VII. DELPHONINE

N. K. Abubakurov and S. Yu. Yunusov

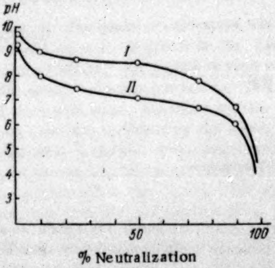
Continuing our work with the alkaloids of Delphinium rotundifolium Afan., we found in this plant, in addition to those isolated earlier [1], still another crystalline alkaloid. Its presence could be shown only after the mother liquors from the delsemine and delsemidine were saponified and the alkamine portion of the hydrolysis products was subjected to fractional separation on the basis of difference in basicity. Purification and individualization of the alkaloid are associated with a number of difficulties. The problem is that the alkaloid does not lend itself to recrystallization from any of the ordinary organic solvents. It can be obtained in a crystalline form only by its precipitation from acid solutions with an excess of either ammonia or alkali.

Another unusual property of the alkaloid, making it difficult to work with, , was the fact that its solubility in water did not increase with elevation of the temperature, and on the contrary dropped – a property already observed for the alkaloid delphatine [2]. We were unable to obtain any crystalline salts of the alkaloid. On comparing the physicochemical constants, the character of the functional groups and the analytical data for the isolated base with the properties of other aconite alkaloids we found that it comes closest to the amino alcohol of the long and well known alkaloid delphinine. The table given below is presented to support the identity of the two alkaloids:

Indices	Our data	Data of Craig, Jacobs, et al.[3]	Data of Schneider
Melting point	79-80°	76-78°	78.5°
Specific rotation	+37.7°	+37.5°	+37.88°
Functional groups	3OH, $4OCH_3$	3OH, $4OCH_3$	3OH, $4OCH_3$
Amount of C (in %)	63.73, 63.54	63.44	62.87
Amount of H (in %)	8.89, 9.02	8.37	8.92

Previous investigators gave the alkamine the name delphonine, and we retained this name. The amount of delphonine in the roots and aboveground organs of D. rotundifolium is approximately the same and does not exceed 0.06-0.08% of the plant weight. D. staphisagria, still being the only source of delphinine, does not in the Soviet Union territory [5], and the finding of the alkamine portion of one of the first discovered and repeatedly described alkaloids is not without interest. We attempted to find delphinine also among the alkaloids of D. rotundifolium, but although these attempts proved unsuccessful, and in the acid hydrolyzates after saponification of total alkaloids, we were unable to show the presence of either acetic or benzoic acid (the hydrolyzates were composed mainly of delseminic and delsemidinic acids and their decomposition products), still the possibility is not excluded of finding the original, etherified compound of delphonine in plants.

In recent yeats the alkaloids of D. staphisagria have been studied chiefly by Jacobs and coworkers. Mainly on the basis of the analyses of delphinine [6], for which the most acceptable formula was found to be $C_{33}H_{45}O_9N$, they indicated for its alkamine portion the composition $C_{24}H_{39}O_7N$. Schneider agreed with this formula. The availability of a sufficient amount of the lower molecular delphonine, in addition obtained in the crystalline form for the first time, caused us to again return to an examination of its formula. Here the problem was to decide between C_{24} and C_{25}. The substance lent itself with difficulty to combustion, and the analytical data were contradictory. On the whole the values obtained for the carbon content were in the direction of favoring the C_{24} formula. However, as in the case of delphatine [2], it was the potentiometric titration results that proved decisive. The alkaloid equivalent was repeatedly checked with fairly good agreement and accuracy. It proved to be equal to 470 ± 1, which in combination with the elementary analysis data, corresponds to the formula $C_{25}H_{41}O_7N$. Consequently, the formula $C_{34}H_{47}O_9N$ should be assigned to delphinine, already proposed for it in earlier studies [7].



The dissociation constant of delphonine was the subject of a different type of discussion on the nature of the heterocyclic ring in aconite alkaloids. The American authors [3] found a pK of 10.02 for delphonine, and explained the increased basicity of the alkaloid as being due to the presence of a system of two conjugated double bonds connected in a definite manner with the nitrogen atom. In our determinations the pK of delphonine proved to be considerably lower, and specifically 7.1. As a base, delphonine is somewhat weaker than delsine (see Figure), and in accord with this, when their mixture is separated on the basis of decreasing basicity it deposits from the fractions following the delsine fractions (pK 8.5 in water solution).

In general the values of the dissocation constant of delsine and delphonine are of the same order and differ but slightly from those of alkaloids of the tropane, morphine and other series, i.e. those alkaloids in which the tertiary amino nitrogen is found in the hydrogenated cyclic ring and does not have adjacent double bonds.

The results of determining the N-alkyl group of delphonine * proved unexpected. Jacobs and Craig [6] fused delphinine with potassium hydroxide at 260° and trapped methylamine in the volatile reaction products, which they identified as the picrate. Several years later it was again stated [9] the the N-alkyl group of delphinine, provided it was present, should be the methyl. This time the alkyl group was cleaved as methyl iodide and trapped in an alcohol solution of trimethylamine. However, when compared with the calculated, the low values of the analytical determinations and other considerations caused the authors to doubt the reliability of the obtained results. The theory was expressed that the aconite alkaloids, in particular delphinine [10], in general do not contain N-alkyl groups and that the carbon atoms, here determined as an alkyl group, are actually only a link between the tertiary nitrogen atom, situated at the junction of two rings, and the rest of the molecule. The later studies of the authors on delphinine [11] gave no evidence that their opinion on the matter had changed.

We oxidized delphonine with potassium permanganate in sulfuric acid solution. The volatile reaction products were distilled and condensed with dimedon; here two products were obtained. The first of them, obtained greater amount, was identical with the condensation product of dimedon with formaldehyde; the second, obtained in smaller amount, was determined to be the anhydride of the condensation product of dimedon with acetaldehyde so that here also we were unable to obtain a satisfactory solution to the problem. The problem was solved only by the resynthesis of the N-alkyl portion of the alkaloid (I).

As in the case of delsine, nitrous acid was used to oxidize the C-alkyl atoms. In itself this is a well known reaction; however, here it was complicated by secondary phenomena associated with the extreme sensitivity shown by the other elements in the molecule to oxidation; consequently, the yield of the nitroso product (II) did not exceed 20-25%. From the literature it is known that other aconite alkaloids also give nitroso products when treated with nitrous acid in hot acetic acid solution. In particular, the nitroso compounds of delphinine and aconitine [12] have been described. If nothing else, the fact that neither of these compounds contained any appreciable amount of N-alkyl groups is evidence that they were nitroso-substituted nor-bases. However, Jacobs and Craig considered their compounds in a different light: specifically as nitroso derivatives of secondary amines with the same number of carbon atoms, and formed as the result of alkaloid isomerization. In the light of new

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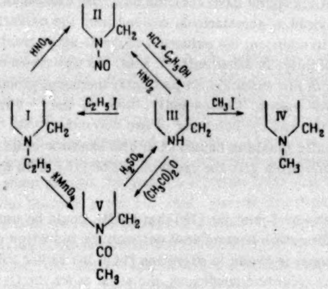
* Preliminary data on the character of the N-alkyl group of delphonine were published earlier [8]. Here they are supplemented by additional experimental material.

data the nitrosonordelphinine should have the formula $C_{32}H_{42}O_{10}N_2$ (instead of $C_{33}H_{44}O_{10}N_2$), and nitrosonoraconitine $C_{32}H_{42}O_{12}N_2$ (instead of $C_{34}H_{44}O_{13}N_2$). The analytical data are fully comparable.*

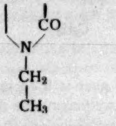
The N-nitroso compound of delphonine (II) was reduced to the nor-base (III). The secondary nature of the amino nitrogen was supported by regaining in the usual manner the nitroso compound (II) and the acetyl derivative (V). Nordelphonine, the same as nordelsine, and even lacking an N-alkyl group, continues to cleave an aldehyde when oxidized, but here only formaldehyde.



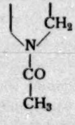
The nor-base was alkylated in turn with methyl iodide and with ethyl iodide. A new base (IV) was obtained in the first case, and was different from delphonine. In the second reaction, Product (I) was obtained in good yield, and was identical with natural delphonine.

There is still another known delphonine derivative, namely N-methyl-des-delphonine [3, 4], that in the character of the nitrogen is closely associated. As yet nobody has been able to effect complete decomposition (by Hofmann degradation) of the aconite alkaloids, and consequently the communication of Schneider [4] that he was able to obtain a nitrogen-free derivative of delphonine would seem to be promising much. We repeated Schneider's experiment on the preparation of the delphonine methiodide. However, neither with his method, nor in a sealed tube, were we able to obtain the delphonine quaternary compound.

We also studied some of the oxidation products of delphonine. The oxidation of delphonine with permanganate in acetone, the same as for other aconite alkaloids, leads to the formation of neutral products of a lactam nature. In practice it is possible to form two isomeric substances: an α-form with the carbonly group in the ring and an α'-form with the same group in the chain.



α-Oxodelphonine



α'-Oxodelphonine

The reaction products did not lend themselves to separation by the usual methods. Assuming that here we were dealing with a mixture of two isomers, we subjected the neutral fraction to saponification. Here we expected

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[*] Found [12] for the nitroso compound of delphinine in %: C 62.85, 63.24; H 7.11, 6.94; N 4.19; OCH_3 20.07. $C_{32}H_{42}O_{10}N_2$. Calculated %: C 62.52; H 6.89; N 4.56; OCH_3 20.20. Found for the nitroso compound of aconitine in %: C 59.04, 59.18; H 6.54, 6.67; OCH_3 18.68, 18.22. $C_{32}H_{42}O_{12}N_2$. Calculated %: C 59.43; H 6.55; OCH_3 19.20.

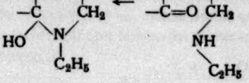
that the α'-form would be saponified to a secondary amine, while the α-form would either remain unchanged or go to the amino acid. Actually, we isolated two crystalline compounds from the saponification products: one of basic character, identified with nordelphonine; the second of neutral character, in its properties most resembling α-oxodelphonine. The analysis data for the latter compound, including the determination of the alkylimide group, lead to the formula $C_{25}H_{39}O_8N$, supporting the fact that all of the carbon atoms of the original alkaloids were retained.

In the literature on aconite alkaloids the opinion long prevailed that the formation of neutral oxo compounds is of necessity associated with the cleavage of the N-alkyl group either as acetaldehyde (in the case of NC_2H_5) or as formaldehyde (in the case of NCH_3). Recently, especially after the work with lycoctonine [13], more and more facts [14, 15] that refute this viewpoint have accumulated. We examined a considerable number of papers and became convinced that the yield of acetaldehyde derived from the oxidation of an N-ethyl group rarely exceeded 10-15% of the theoretical. In addition, the oxidation of the N-alkyl group with permanganate is run under different conditions, and specifically, in dilute sulfuric acid. As was shown on the example of nordelsine and nordelphonine, other elements in the molecule, in particular methoxyl groups, at times cleaving as methanol, can also serve as the formaldehyde source. Consequently, there is not any essential contradiction between the observed cleavage of aldehydes and the obtaining of oxo derivatives with the same number of carbon atoms. New data on the oxidation of aconite alkaloids caused us to also examine other generally known facts. Thus, if it is true that aconitine and mesaconitine give the same oxonitine [16], then the very existence of the alkaloid mesaconitine becomes doubtful.

It was recently indicated by Schneider [18] that $LiAlH_4$ could be used to transform oxonitine into noraconine. Obviously, this transformation is associated not with the reduction of a lactam carbonyl, as is postulated by Schneider (a lactam carbonyl is absent in oxonitine [14]), but rather with the presence of an N-acetyl group in oxonitine, which under the reduction conditions, the same as for the O-acetyl and O-benzoyl groups, is easily cleaved. A similar objection should also be made with respect to the interpretation given by the authors [19] relative to the character of the oxidation products of delphinine and delphonine.

It seems timely to mention that NO- and CO-derivatives, obtained by the oxidation of an N-alkyl group (nitrosonordelsine, nitrosonordelphonine, α'-oxodelphonine, oxonitine, oxoaconitine), show a specific rotation that is the opposite of the original alkaloid. In those cases where a cyclic methylene group with an adjacent nitrogen atom (lycoctonine, oxodelsine, α-oxodelphonine) is oxidized, the sign of rotation does not change. If this is not accidental, then continuing the analogy, it could be predicted that the α-oxodelphinine of Jacobs and Craig [6] is the N-acetyl derivative of nordelphinine, while the β-oxodelphinine is the normal cyclic lactam.

Still another circumstance draws attention. When etherlike alkaloids (aconitine, delphinine) are oxidized, the N-acetyl derivatives predominate in the reaction products. When amino alcohols (lycoctonine, delphonine) are oxidized, the lactams appear as the main reaction product.



The shaking of delphonine with freshly prepared silver oxide gave still another oxidation product — hydroxydelphonine. This reaction was reminiscent of the formation of hydroxylycoctonine from lycoctonine [13, 17]. Edwards and Marion assume that hydroxylycoctonine, similar to pseudostrychnine, is a carbinolamine. With all the allure of such a postulation, the arguments presented by the Canadian authors cannot be considered fully convincing. The chief objection consists in the fact that hardly any specific reactions were cited to show the presence of a tautomeric system in hydroxylycoctonine.

In particular, it is not clear why neither a carbonyl group nor a secondary amino nitrogen appears, whereas pseudostrychnine, despite a fairly dense packing of the multicyclic system, gives without hindrance both the N-nitrosoamine and the N-acetyl derivative. Not disputing the possibility of cleaving ethylamine from hydroxylycoctonam, it should be mentioned that under resinification conditions such cleavage could have also proceeded for a different reason.

The experimental material presented here clearly illustrates the presence of a tight bond between delsine and delphonine. Both alkaloids were isolated from the same plant, have the same composition, and give a number of derivatives with similar properties. This sharing of properties is so striking that involuntarily the suspicion arose that delsine (by analogy with atisine) could be isomerized by hot alkali to delphonine. The experiment on the isomerization of delsine gave a negative result, in this way confirming the fact that delsine and delphonine are natural isomers.

EXPERIMENTAL

Delphonine

Fifty grams of mixed bases, obtained in the saponification of the delsemine and delsemidine mother liquors, was dissolved in ether, and after separating the small amount of delsine that precipitated here, the mixture was separated into 10 fractions by successive extraction with 0.5N H_2SO_4 on the basis of decreasing basicity. The acid fractions (the volume of each was 20 ml) were made alkaline with ammonia. The first three fractions immediately gave needlelike crystals, which were identified as delsine. The 4th and 5th fractions represented oily substances with a thin inclusion of crystals. Coarse platelike crystals slowly began to grow at the interface of the ammonia solution with the acid when the 6th, 7th and 8th fractions were allowed to stand. A friable amorphous precipitate deposited from the fractions 9 and 10; this was not investigated further. The crystals from the 6th, 7th and 8th fractions were dissolved in 30 ml of 1 N sulfuric acid and by fractional precipitation with the calculated amount of ammonia, were again fractionated, but this time on the basis of increasing basicity. In this way 5 fractions were obtained, the first and last of which were discarded, while the middle fractions represented pure delphonine. By repeating the operations, the original 4th and 5th fractions can again be separated into delsine and delphonine.

For better purification the crude delphonine was recrystallized once more by precipitation. The nearly colorless crystals were crushed, covered with cold water, and the saturated solution obtained on standing was transferred to a thermostat at 40°. After some time crystals deposited from solution. Delphonine crystallizes either as needles or as large hexagonal prisms. It is possible that its crystal lattice contains one molecule of water, since when vacuum-dried the freshly crushed crystals lose up to 3.5% of their weight. With the exception of petroleum ether, the base is readily soluble in all of the usual organic solvents, including ether. Quite readily soluble in cold water (1.7:100 at 20°). M.p. 79.5-80.5°.

0.2014 g substance in 10 ml ethanol, $\underline{1}$ 10.0, α_D +0.76°, $[\alpha]_D^{26}$ +37.7°.

2.430, 3.230 mg substance: 5.675, 7.520 mg CO_2; 1.930, 2.605 mg H_2O. 4.191, 8.603 mg substance: 0.110 (20°, 729 mm), 0.241 (24°, 728 mm) ml N_2. 0.1354, 0.1402 g substance: 20.30, 20.55 ml CH_4 (0°, 760 mm). 11.042, 9.175 mg substance: 11.01, 9.14 (for OCH_3), 2.83, 2.52 (for NC_2H_5) ml 0.05 N $Na_2S_2O_3$. 0.4542, 0.3707, 0.7693 g substance: 9.64, 7.89 (potentiometrically), 16.38 (methyl red) ml 0.1 N. HCl. Found %: C 63.73, 63.54; H 8.89, 9.02; N 2.88, 3.02; OH 11.45, 11.20; OCH_3 25.78, 25.76; NC_2H_5 9.19, 9.85; equiv. 471.2, 469.8, 469.6. $C_{25}H_{41}O_7N$. Calculated %: C 64.24; H 8.84; N 3.00; 3OH 10.91; 4OCH_3 26.55; NC_2H_5 9.21; equiv. 467.6. $C_{24}H_{39}O_7N$. Calculated %: C 63.55; H 8.67; N 3.09; equiv. 453.6.

A solution of 0.5 g of delphonine in 10 ml of 30% acetic acid was reduced in the presence of platinum catalyst. The amount of hydrogen absorbed in 3 hours was very small. The starting delphonine was recovered when the solution was made alkaline.

For isomerization, 1.0 g of delsine was heated for 4 hours in 10 ml of 20% methanolic KOH solution. No change as the result of reaction was observed, and after we evaporated the alcohol, the delsine was recovered completely.

The ionization constants of delsine and delphonine were determined electrometrically, using a hydrogen electrode of the Benker type. The calomel electrode with saturated potassium chloride solution was taken as a standard. The measurements were made in water solution and in 50% ethanol solution. Saturated solutions of the alkaloids were prepared for the measurements in water: 0.006N for delsine and 0.035 N for delphonine. The solutions were titrated with 0.1 N hydrochloric acid. The results of the measurements in water solution are shown in the figure. In dilute alcohol solution the half-neutralization point was found to be at pH 8.3 for delsine, and at pH 6.8 for delphonine.

N-Alkyl Group of Delphonine

Determination of the N-alkyl group by oxidation. To an ice-cooled solution of 2.0 g of delphonine in 20 ml of 5% H_2SO_4 was added in two hours, with stirring, a solution of 0.90 g of potassium permanganate in 25 ml of water. After we decolored the solution and filtered the manganese dioxide precipitate we distilled the colorless filtrate into an an ice-cooled receiver. To the distillate was added 50 ml of a warm 1% water solution of dimedon. The solution was heated for 10-15 minutes on the water bath; here a voluminous flocculent precipitate was obtained, gradually turning into crystals. Yield 70 mg. When recrystallized from 1.5 ml of petroleum ether the crystals separated into two portions. The portion readily soluble in petroleum ether (20 mg) had m.p. 186° and after a second recrystallization from alcohol did not depress the melting point when mixed with the condensation product of formaldehyde and dimedon (m.p. 189°). The portion difficulty soluble in petroleum ether, and not having a sharp melting point, was dissolved in 5 ml of alcohol and after adding 2 ml of 1 N hydrochloric acid solution was heated on the water bath for 2 hours. Crystals were obtained when the alcohol was evaporated. They were washed with 5% sodium hydroxide solution and then recrystallized from dilute alcohol. Yield 16 mg. M.p. 174°. Its mixed melting point with the anhydride of the condensation product from acetaldehyde and dimedon (m.p. 175°) was not depressed.

N-Nitrosonordelphonine. To a solution of 14.6 g of delphonine in 300 ml of 50% acetic acid was added 150 ml of 60% sodium nitrite solution in 1.5 hours with simultaneous heating on the boiling water bath. The cooled solution was neutralized with sodium carbonate. The unreacted delphonine was extracted with ether. Then the solution was saturated with potash and extracted several times with chloroform. The chloroform solution was distilled to a small volume. The remainder of the solvent was removed by repeated evaporation with water and methanol. The nitroso derivative deposited on the bottom of the dish as compact clusters of crystals when the aqueous methanol solution was allowed to evaporate slowly (in the air). Yield 3.1 g.

When recrystallized from extremely dilute methanol the N-nitrosonordelphonine was obtained as coarse prisms or clusters of prisms with ill-defined edges. With phenol and sulfuric acid the substance gives a distinct test for the nitroso group. M.p. 175°.

0.2090 g substance, in 10 ml ethanol, $\underline{1}$ 10.0, $\alpha_D - 1.35°$, $[\alpha]_D^{25} - 64.6°$.

4.486, 4.795 mg substance: 9.625, 10.219 mg CO_2; 3.119, 3.379 mg H_2O. 5.990, 5.820 mg substance: 0.320 (19.5°, 734 mm), 0.304 (14.5°, 737mm) ml N_2. Found %: C 58.55, 58.16; H 7.78, 7.89; N 5.88, 5.91. $C_{23}H_{36}O_8N_2$. Calculated %: C 58.96; H 7.74; N 5.98.

Nordelphonine. A solution of 1.44 g of nitrosonordelphonine in 25 ml of ethanol was saturated with HCl gas with external ice-salt cooling to −12°. The reaction mixture was kept in a sealed tube for 2 days at room temperature, and then was evaporated in vacuo. The residue was dissolved in 20 ml of water and after neutralization with soda the neutral products were extracted with chloroform. Then the aqueous solution was made strongly alkaline with ammonia and again extracted with chloroform (products of basic character). The chloroform solutions were distilled separately. The reaction products were dissolved in water, the aqueous solutions freed of tar, and then evaporated on the water bath. Any residual water was removed by drying over calcium chloride. The yield of neutral products was 0.43 g, and that of the basic products 0.77 g. The product of neutral character was obtained as a brownish mass. The product of basic character crystallized on standing.

When recrystallized from a very small amount of water, the nordelphonine is obtained as compact clusters of slender needles. It crystallizes with one molecule of water, which can be easily removed by drying at 50-60°. The base is exceedingly soluble in water, the alcohols and chloroform. M.p. 95-96°.

0.2592 g substance in 10 ml ethanol, $\underline{1}$ 10.0, $\alpha_D + 1.07°$, $[\alpha]_D^{23} + 41.3°$.

3.962, 3.125 mg substance: 9.066, 7.135 mg CO_2; 3.059, 2.469 mg H_2O. 4.165 mg substance: 0.124 ml N_2 (17.5°, 733 mm). Found %: C 62.45, 62.31; H 8.64, 8.84; N 3.30. $C_{23}H_{37}O_7N$. Calculated %: C 62.85; H 8.48; N 3.19.

A solution of 80 mg of nordelphonine in 3 ml of 10% sulfuric acid was treated with 1 ml of 60% $NaNO_2$ solution. After a day, the solution was made alkaline with soda and then extracted with chloroform. The chloroform was distilled, and the residue (52 mg) was recrystallized from 1 ml of water. Crystals with m.p. 174-175° were obtained, completely identical with nitrosonordelphonine.

In exactly the same manner as for determination of N-alkyl group, 0.32 g of nordelphonine was oxidized with 0.30 g of potassium permanganate. Here 10 mg of the condensation product of formaldehyde with dimedon was obtained (m.p. 186-187°).

N-Methylnordelphonine. A solution of 240 mg of nordelphonine in 5 ml of methanol was treated with 0.5 ml of methyl iodide and then the mixture was heated in a sealed tube on the boiling water bath for 1.5 hours. The excess methyl iodide and methanol were evaporated to dryness. The residue was dissolved in 2 ml of water, the solution acidified with 3 drops of dilute sulfuric acid, and the small amount of iodine that separated here was removed. The clear filtrate was treated with 0.3 ml of concentrated ammonia solution. On standing, coarse crystals of methylnordelphonine separated from solution. Yield 215 mg. Methylnordelphonine is purified by repeated precipitation from acid solution and by recrystallization from water heated to 80°. Its solubility in water, the same as for delphonine, decreases with temperature increase. When dried in vacuo the base loses up to 4.0% of its weight, which apparently is associated with the presence of one molecule of crystallization water. M.p. 146-147°.

0.0898 g substance in 10 ml ethanol, $\underline{1}$ 10.0, α_D +0.35°, $[\alpha]_D^{22}$ +39.0°.

4.962, 3.586 mg substance: 11.468, 8.246 mg CO_2; 3.786, 2.714 mg H_2O. 11.575. 9.560 mg substance: 11.90, 9.98 ml 0.05 N. $Na_2S_2O_3$. Found %: C 63.07, 62.75; H 8.54, 8.47; OCH_3 26.58, 27.00. $C_{24}H_{39}O_7N$. Calculated %: C 63.55; H 8.67; OCH_3 27.40.

N-Ethylnordelphonine. A solution of 130 mg of pure nordelphonine in 3 ml of ethanol was mixed with 0.2 ml of ethyl iodide and the mixture heated on the water bath for 2 hours. The excess ethyl iodide and ethanol were evaporated in vacuo to dryness. The residue was dissolved in 1.0 ml of water, the solution made acid, filtered from iodine, and made alkaline with ammonia. After some time crystals of the base begin to grow at the interface of the ammonia and acid solutions. The next day the crystals were separated (yield 105 mg) and recrystallized in the usual manner for delphonine, i.e. by heating the cold saturated water solution. Crystals with m.p. 79-80° were obtained. They showed a sharp melting point at the same temperatures when mixed with authentic delphonine.

$[\alpha]_D^{23}$ +37.1° (c 0.87, in ethanol).

Found %: C 63.70; H 9.02. $C_{25}H_{41}O_7N$. Calculated %: C 64.24; H 8.84.

Delphonine and Methyl Iodide. A suspension of 1.0 g of delphonine, 0.1 g of sodium bicarbonate, 3 ml of methyl iodide and 20 ml of water was heated on the water bath for 12 hours. Here the delphonine did not dissolve and the deposition of a yellow substance was not observed. After distilling off the methyl iodide the water-insoluble crystalline precipitate was separated. It proved to be the original base. Evaporation of the water solution also gave delphonine.

A solution of 0.3 g of delphonine and 0.5 ml of methyl iodide in 5 ml of methanol was heated in a sealed tube at 100° for 2 hours. After removal of methyl iodide the methanolic solution was treated with ether. Here a very small amount of brownish oil was obtained. The latter was dissolved in water, the solution separated from iodine, and then made alkaline with ammonia. Here crystals were obtained (42 mg), which proved to be identical with the original base. Evaporation of the ether-methanol solution gave another 210 mg of delphonine.

Oxidation of Delphonine

Delphonine and $KMnO_4$. Powdered potassium permanganate was added in small portions (0.25-0.30 g) to a solution or 3.09 g of delphonine and 10 ml of glacial acetic acid in 60 ml of dry acetone. Each fresh portion of reagent was added only after the previous one had been decolorized. About 1.5 g of oxidizing agent was consumed in 30 minutes. The oxidation was accompanied by self-heating. The decolorization of the last 0.30 g portion required 2.5 hours. The total reaction time was 4 hours. The total consumption of $KMnO_4$ was 2.14 g, which calculated on the basis of equivalent weights corresponds to oxidation with approximately 1.5 moles of oxygen. The manganese dioxide precipitate was filtered and washed with fresh acetone solution. Together with the brown oxide a small amount of crystals remained on the filter, and proved to be potassium acetate. The combined acetone solution was evaporated to dryness. The residue was dissolved in 30 ml of water. The reaction products were separated into basic, neutral and acid fractions. For this the water solution was repeatedly extracted with chloroform (acid and neutral products), after which it was made alkaline with ammonia and again extracted with chloroform (products of basic character). The chloroform solution with neutral and acid products was shaken with 5 ml of saturated sodium carbonate solution. The soda solution was washed with chloroform, acidified with sulfuric acid, and the liberated products of acid character taken up in chloroform. After distillation and complete removal of the chloroform we obtained 0.085 g of the basic fraction, 2.633 g of the neutral and 0.108 g of the acid fraction. By preparing the nitroso derivative we showed that the products of basic character contain a small amount of nordelphonine. The acid products were not studied in detail.

Saponification of oxo compounds. The neutral fraction (1.47 g) from the preceding experiment was dissolved in 10 ml of 2N sulfuric acid and heated on the water bath for 3 hours. The solution, prior to heating showing negative reaction with silicotungstic acid, on conclusion of reaction gave a copious precipitate with it. In the manner described above the reaction mixture was separated into products of basic, neutral and acid character. The only difference here was that the products of neutral and acid character were first extracted with ether, and then chloroform. The products of basic character (68 mg) began to crystallize when their water solution was dried. Here it proved difficult to separate the crystals, and with aid of 3 ml of 30% $NaNO_2$ and 3 ml of 10% H_2SO_4 they were converted into the nitroso compound. We obtained 46 mg of crystalline substance with m.p. 173°. Its mixture with nitrosonordelphonine did not show a melting point depression.

α-Oxodelphonine. The ether solution with the products of neutral and acid character was extracted with 2 ml of saturated sodium carbonate solution, dried over potash, and condensed. Crystals deposited from solution when the ether was allowed to evaporate slowly. When recrystallized from methanol they were obtained as small transparent tablets with a nearly perfect square shape. Yield 105 mg. Another 30 mg of α-oxodelphonine was obtained from the chloroform solution of the neutral and acid products. M.p. 197-198°.

0.1200 g substance in 10 ml ethanol, $\underline{1}$ 10.0, α_D +0.26°, $[\alpha]_D^{25}$ +21.7°.

2.958, 3.058 mg substance: 6.788, 7.048 mg CO_2; 2.042, 2.186 mg H_2O. 6.380, 7.168 mg substance: 6.30, 7.24 ml 0.05 N. $Na_2S_2O_3$ (for OCH_3). 8.180 mg substance: 1 86 ml 0.05 N. $Na_2S_2O_3$ (for NC_2H_5). Found %: C 62.62, 62.90; H 7.72, 8.00; OCH_3 25.54, 26.12; NC_2H_5 8.15. $C_{25}H_{39}O_8N$. Calculated %: C 62.35; H 8.16; $4OCH_3$ 25.78; NC_2H_5 8.94.

α'-Oxodelphonine. (N-acetylnordelphonine). A solution of 0.30 g of nordelphonine in 3.0 ml of acetic anhydride was heated for 2 hours at 100°. The excess anhydride was decomposed with water. The reaction products were separated in the usual manner into a neutral, basic and acid fraction. The residue from the distillation of the chloroform solution with neutral products was dissolved in water, filtered, reduced to small volume, and dried in a vacuum-desiccator over calcium chloride. Here 0.29 g of glassy substance was obtained, readily crushed to a light-colored powder. Prior to analysis the substance was vacuum-dried a second time at 60°. Although we did not obtain the α'-oxodelphonine in crystalline form, here it is important to take notice of: the reverse sign of rotation shown by α-oxodelphonine and the authentic absence of an N-alkyl group. M.p. 88-92°.

0.1160 g substance in 10 ml ethanol, $\underline{1}$ 10.0, α_D − 0.27°, $[\alpha]_D^{17}$ − 23.3°.

3.528, 2.986 mg substance: 7.998, 6.752 mg CO_2; 2.586, 2.164 mg H_2O. 5.898, 6.235 mg substance: 5.70 6.07 ml 0.05 N. $Na_2S_2O_3$. Found %: C 61.87, 61.71; H 8.20, 8.11; OCH_3 24.99, 25.18. $C_{25}H_{39}O_8N$. Calculated %: C 62.35; H 8.16; $4OCH_3$ 25.78.

Hydroxydelphonine. A suspension of 2.0 g of pure delphonine and 2.0 g of freshly precipitated silver oxide (from 3.0 g of $AgNO_3$ and 2.0 g of KOH) was agitated on a shaker for 6 hours. The delphonine gradually dissolved, and a silver mirror formed. The solution was let stand overnight, and then separated from the silver. Slow evaporation of the water at 40-45° gave a mixture of coagulated silver and crystals. The solution was evaporated to dryness, and the obtained crystals were dissolved in ether. The ether was distilled. The residue (2.0 g) was recrystallized from water. As for all delphonine derivatives, the solubility of the hydroxydelphonine proved to be considerably greater in cold water than in hot. The simplicity of preparation, combined with excellent yield and crystallization ease, permit recommending hydroxydelphonine as a trustworthy derivative fo for the identification of delphonine. Hydroxydelphonine is readily soluble in cold water, the alcohols, chloroform and ether. Prior to analysis the substance was substance was dried. M.p. 127-128°.

0.2064 g substance in 10 ml ethanol, $\underline{l}$ 10.0, α_D +0.23 ∓ 0.04°, $[\alpha]_D^{18}$ +11 ∓ 2°.

4.156, 3.968 mg substance: 9.404, 8.988 mg CO_2; 3.026, 2.920 mg H_2O. 0.2035 g substance: 4.25 ml 0.1 N HCl (potentiometrically). Found %: C 61.75, 61.82; H 8.15, 8.23; equiv. 478.8 $C_{25}H_{41}O_8N$. Calculated %: C 62.09; H 8.13; equiv. 483.6.

SUMMARY

1. The alkaloid delphonine was found in Delphinium rotundifolium, earlier known as the alkamine portion of delphinine. The corrected formula $C_{25}H_{41}O_7N$ is proposed for delphonine.

2. The presence of an N-ethyl group in delphonine was shown by resynthesis of the N-alkyl portion.

3. Some of the oxidation products of delphonine were studied: α-oxodelphonine, α'-oxodelphonine and hydroxydelphonine. It was shown that the formation of oxo compounds of delphonine proceeds predominantly without cleavage of the carbon atoms in the N-alkyl group.

LITERATURE CITED

[1] S. Yu. Yunusov and N. K. Abubakirov, J. Gen. Chem. 21, 967 (1951) (T.p. 1059);* 22, 1461 (1952) (T.p. 1503).*

[2] N. K. Abubakirov and S. Yu. Yunusov, J. Gen. Chem. Suppl. II, 1453 (1953).

[3] L. C. Craig, L. Michaelis, S. Granick and W. A. Jacobs, J. Biol. Chem. 154, 293 (1944).

[4] W. Schneider, Arch. Pharm. 283, 86, 281 (1950).

[5] V. S. Sokolov, "Alkaloid bearing plants of the USSR," Plants of the USSR (Acad. Sci. USSR Press, 1952), p. 206.

[6] W. A. Jacobs and L. C. Craig, J. Biol. Chem. 127, 361 (1939); 128, 431 (1939).

[7] T. Walz, Arch. Pharm. 260, 9 (1922); O. Keller, Arch. Pharm. 263, 274, 280 (1925); L. N. Markwood, J. Am. Pharm. Assoc. 16, 928 (1927).

[8] N. K. Abubakirov and S. Yu. Yunusov, Proc. Acad. Sci. Uzbek SSR 1954, No. 1, 29; Reference J. Chem. 1954, 41258.

[9] C. F. Huebner and W. A. Jacobs, J. Biol. Chem. 170, 515 (1947).

[10] W. A. Jacobs and C. F. Huebner, J. Biol. Chem. 170, 209 (1947).

[11] W. A. Jacobs and S. W. Pelletier, J. Am. Chem. Soc. 76, 161 (1954).

[12] W. A. Jacobs and L. C. Craig, J. Biol. Chem. 136, 303, 323 (1940).

[13] O. E Edwards and L. Marion, Can. J. Chem. 30, 627 (1952); 32, 1146 (1954).

[14] W. A. Jacobs and S. W. Pelletier, J. Am. Chem. Soc. 76, 4048 (1954).

[15] R. C. Cookson and M. E. Trevett, Chem. and Ind., 1954, 1324.

[16] R. Majima and H. Suginome, Ber. 58, 2047 (1925); S. Morio, Ann. 476, 181 (1929); R. Majima and K Tamura, Ann. 526, 116 (1936).

[17] H. Suginome and K. Ohno, C. A. 46, 1008 (1952).

[18] W. Schneider, Reference Volume (Internation Congress Pure and Appl. Chem. Zurich, 1955), Vol. XIV, 156; Angew. Chem. 67, 654 (1955).

[19] W. Schneider, Ann. 590, 155 (1954).

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SUMMARY

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LITERATURE CITED

[1] [illegible]

[2] [illegible]

[3] [illegible]

[4] [illegible]

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[7] [illegible]

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[9] [illegible]

[10] W. A. [illegible]

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[14] [illegible]

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LETTER TO THE EDITOR

L. K. Mushkalo

A paper by B. M. Mikhailov and I. K. Platova, entitled "The Mannich Reaction in the Thiazole Series", appears in the second number of the "Journal of General Chemistry" for 1956. In this paper the authors described the synthesis of 4-methyl-2-β-(dimethylaminomethyl)-methylthiazole from 2,4-dimethylthiazole, dimethylamine hydrochloride and paraformaldehyde in alcohol solution. In the literature section the authors of the paper indicate that the Mannich reaction in the thiazole series had not been described previously. Despite this, as early as 1949 in the paper "Synthesis of Amines in the Thiazole Series," published in the "Ukrainian Chemical Journal" (Vol. XV, p. 467), we studied this reaction in the thiazole, benzothiazole and α-naphthothiazole series. In this paper we described the synthesis of the above mentioned amine under the name of 4-methyl-2-dimethylamino-ethylthiazole by the method reproduced by B. M. Mikhailov and I K. Platova. However, the authors completely fail to mention our paper.

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